CHANGES IN PHYSICAL, HYDRAULIC AND MICROSTRUCTURAL PROPERTIES OF CLAYS EXPOSED TO ORGANICS

KAVITHA SUBRAMANIAM

CHANGES IN PHYSICAL, HYDRAULIC AND MICROSTRUCTURAL PROPERTIES OF CLAYS EXPOSED TO ORGANICS

BY

©KAVITHA SUBRAMANIAM, B. TECH.

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING

FACULTY OF ENGINEERING AND APPLIED SCIENCE

MEMORIAL UNIVERSITY OF NEWFOUNDLAND

ST. JOHN'S NEWFOUNDLAND CANADA

ISBN 0-612-17651-7

Abstract

The use of engineered clay liners for containing landfill wastes and protecting groundwater quality is based on the adsorption capacity and impermeability of the clay fabric. Excessive leachate through clay barriers is mainly due to changes in the intrinsic permeability of the clay material when exposed to contaminants. The compatibility of clay barriers with leachate is also evaluated through an assessment of changes in the index properties and/or internal structure of the soil. One of the major factors that can affect the clay performance is the presence of organic chemicals in the leachate that typically constitute more than 55% of the total leachate generated in landfills.

The goals of this work are to provide a better understanding of the effects of various organic fluids on clay minerals and to provide a database for clay-organic fluid interactions, so that the results may be used for the evaluation and prediction of clay barrier performance in waste containment applications.

Three clay minerals; kaolinite, illite and smectite are investigated in this study. The chemicals used as permeants cover a wide range of dielectric constants and aqueous solubilities. These include acetic acid (acidic), aniline (basic), methanol and acetone (neutral polar), and carbon tetrachloride, trichloroethylene and xylene (neutral nonpolar). Permeability measurements have been carried out on the clays using a rigid wall permeameter. Microstructures have been observed using

Scanning Electron Microscopy to determine the effects of these organic chemicals on the internal structure of the clays. This study also attempts to correlate in dex property tests and sedimentation analyses with observed changes in intrinsic permeability and microstructure of the clays. Electrical properties of the perme ant appear to control hydraulic conductivity and microstructure, especially for smectitic clay.

I dedicate this thesis to my wonderful parents,

Mr. R. Subramaniam

Mrs. Rajalakshmi Subramaniam

Acknowledgements

A number of people have been instrumental in enabling me to successfully complete my graduate study. First of all, I would like to express my sincere and heartfelt gratitude to my advisor, Dr. Pierre Morin for his excellent guidance and support at all stages of this program. I would also like to thank Dr. R. Seshadri, Dean of Engineering and Dr. J.J. Sharp, Associate Dean, Faculty of Engineering, for their continuous encouragement and support during my M.Eng. program. I am very grateful to the Faculty of Engineering and Applied Science and to the School of Graduate Studies, M.U.N., for the generous financial assistance that I received during my two years here. Thanks are due to Hamill Gillespie, New Jersey; Canada Brick, Ontario; and Canada Clay Products, Saskatchewan for the clay materials supplied by them. I also wish to extend my sincere thanks to my friends, Mr. Prashant Mehrotra and Dr. Yenumula Prasad for reviewing the thesis manuscript and providing useful suggestions. Finally, a very special thanks to my family for their constant encouragement, moral support and love.

Contents

List of Figures

List of Tables

List of Symbols and Acronyms

ϵ_0	Permittivity of Vacuum
γ_s	Unit Weight of Particles (Stokes' Law)
γ_w	Unit Weight of Liquid (Stokes' Law)
μ	Dynamic Viscosity of Test Permeant
ν	Cation Valence
ρ	Density of Test Permeant
Δh	Hydraulic Head Difference (Permeameter)
d	Diameter of Particle (Stokes' Law)
e	Electronic Charge
g	Gravitational Constant
k	Intrinsic Permeability
l	Length of Specimen (Permeameter)
n_0	Electrolyte Concentration
t	Time
v	Volume of Permeant Passed (Permeameter)
A	Cross-Sectional Area of Specimen (Permeameter)
B	Boltzmann Constant
D	Dielectric Constant of Medium
H	Thickness of Diffuse Double Layer

K	Hydraulic Conductivity (Permeability when permeant is not water)
T	Temperature
V	Settling Velocity of Spherical Particles (Stokes' Law)
CTC	Carbon Tetrachloride
FWP	Flexible Wall Permeameter
HSWA	Hazardous and Solid Waste Amendments
RWP	Rigid Wall Permeameter
SEM	Scanning Electron Microscopy
TCE	Trichloroethylene
USEPA	U.S. Environmental Protection Agency
XRD	X-Ray Diffraction

Chapter 1

Introduction

1.1 Importance of Clay-Chemical Interactions in Containment Liner Design

One of the most vital and pressing issues facing modern society today is the contamination of the environment by industrial, domestic and municipal wastes. The advances in technology have increased not only the production capacity of industries, but also the volume of harmful wastes generated and, thereby, the deleterious effects of these substances on the human health and environment. Some scientists have projected an annual total waste generation of as much as 12 billion tons by the year 2000 (Tchobanoglous, 1993). In 1990, Americans

alone generated over 195 million tons of municipal solid waste and the annual amount is expected to increase to more than 220 million tons by 2000 A.D. The safe disposal of hazardous wastes is, therefore, of prime importance when dealing with the issues of global environment sustainability and development.

Of the several disposal techniques available for hazardous wastes, landfilling is the most common. A good approach towards safe disposal of hazardous wastes involves improving the design and construction of the protection clay barriers or liners that are used to encase landfills. The primary purpose of these liners is to impede migration of landfill leachate into groundwater and/or to prevent outwash of waste material by precipitation and runoff water. One of the primary obstacles in designing a good landfill clay liner is a limited knowledge of the complex physico-chemical interactions that might take place between the constituents of landfill leachate and the liner material. The present research work pertains to the study of such interactions as may occur between the leachate and clay liner material, and their implications for hazardous waste disposal and containment.

1.2 Scope and Objectives of the Research

The most common types of materials employed as liners are clays, synthetic geomembranes and sometimes, a combination of both. In this study, only clays are

considered. In chemical waste landfills, one of the most important questions that arises is the ability of clay barriers to effectively contain wastes without undergoing appreciable alterations in microstructure and/or hydraulic conductivity.

One of the major factors that can cause changes in the hydraulic conductivity and microstructure of clays is the presence of organic chemicals in the landfill leachate. Organic chemicals typically constitute more than 55% of the total leachate generated in landfills. Depending on the nature and reactivity of the organic liquids, different physical and chemical reactions occur. These may cause changes in the properties of the clay minerals such as, an increase or decrease in the hydraulic conductivity due to dissolution or precipitation of clay soil particles, or changes in the microfabric due to aggregation or dispersion of particles, or an alteration of mechanical properties such as shear strength, all of which, ultimately affect the performance of the liner material. A good liner is one whose structure and properties are not adversely altered by interaction with the leachate. It is, therefore, obvious that in order to safely contain hazardous waste in a landfill, a sound knowledge of the physical and chemical processes involved must be attained.

Several investigators (Mesri and Olson 1971; Brown et al. 1984; Anderson et al. 1985) have reported increases in hydraulic conductivity of clays, of two or three orders of magnitude when permeated with pure, reagent-grade organic

fluids. Other researchers (Uppot and Stephenson 1989) have shown the increase in conductivity to be just two or three times. Daniel and Liljestrand (1984) showed that permeation of compacted clay with dilute organic waste liquids from chemical waste landfills and impoundments did not cause any detrimental effects. The existing literature, therefore, appears to be of a conflicting nature. This is possibly due to several factors, viz. effect of different types of permeameters, hydraulic gradients, soil core preparation methods and concentration of the organic liquids studied. This study was undertaken with the following objectives:

1. To determine the changes in hydraulic conductivity of selected clay minerals when permeated with organic fluids.

2. To study the alterations in the microfabric of clays due to exposure to organic fluids.

3. To use these measurements and values obtained from literature, such as, dielectric constant and viscosity-density data of the organic fluids, to explain the observed differences in permeability and microstructure of clays with organic chemicals as compared to water.

4. To study the correlation between index property tests and the changes in the hydraulic conductivity and microstructure of the clays.

5. To use the results obtained in this study to present a comprehensive picture of clay-organic interactions for hazardous waste disposal applications.

1.3 Organization of the Thesis

The thesis consists of 5 chapters and appendices, the contents of which are as follows:

- Chapter 1 - **Introduction**: Statement of the problem. The scope and objectives of the research are presented.
- Chapter 2 - **A Review of Literature** on hydraulic conductivity and microstructure analysis, clay-chemical compatibility studies, and state of the art testing methodologies.
- Chapter 3 - Description of the **Materials and Methods** employed in the study.
- Chapter 4 - **Presentation and Discussion of Results** obtained in this experimental study.
- Chapter 5 - **Summary and Conclusions** of the study.

Figure 1.1 is a summary of the test scheme followed in this study.

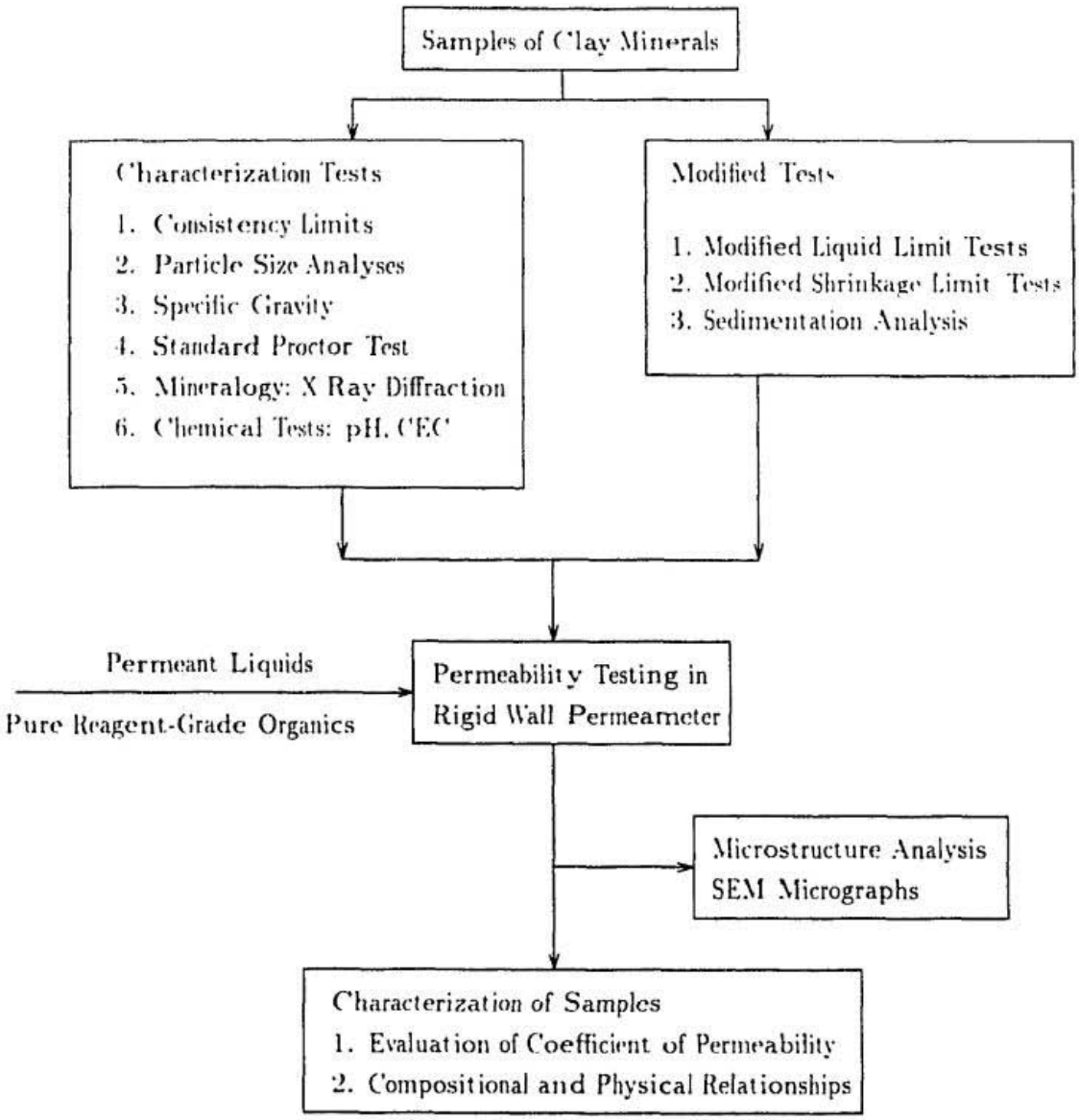


Figure 1.1: Test Scheme Followed in the Study

Chapter 2

Literature Review

The purpose of this chapter is to review the literature pertinent to this investigation. The chapter is divided into four sections. The first section gives an overview of hazardous waste disposal in landfills. A classification of hazardous wastes according to the nature of the waste fluids is presented. The second section discusses at length the typical structure and mineralogical properties of three classes of clays that were used in this study. Some of the major findings of past researchers on clay-chemical interactions and the effects of such interactions on soil permeability are discussed in the third section. Effects of various parameters on hydraulic conductivity measurements is the subject of discussion in the fourth section. The relevance of such studies to the present investigation is discussed in the course of the sections, where applicable.

2.1 Hazardous Waste Disposal in Landfills: An Overview

Design of containment structures for hazardous waste disposal has, of late, been the object of much attention from environmental engineers. Increasing levels of environmental consciousness and case-histories of failures of earth-lined structures have brought this seemingly straight-forward subject under close scrutiny. Hazardous and non-hazardous solid wastes are typically managed in a waste containment structure, frequently referred to as a residue landfill. Alternate techniques in hazardous waste management have progressed further, but 26% of the total volume generated is still managed by land disposal in waste containment landfills (Miller 1980). Materials placed in landfills include such things as municipal garbage and trash, demolition debris, sludge from waste water treatment plants, incinerator ash, foundry wastes and toxic and hazardous materials (Fetter 1993).

Peterson (1983) reported that, in 1983, there were 12,991 landfills in the United States, including 2395 open dumps, and an unknown number of abandoned landfills. Failure of landfills may occur due to a variety of causes such as improper operating methods, defective leachate collection systems, improper consolidation, pumping out of leachate and corrosion of drums containing liquid

wastes. The U.S. Environmental Protection Agency's (USEPA) minimum technological requirements for hazardous waste landfill design and construction were introduced by the Congress in the 1984 Hazardous and Solid Waste Amendments (HSWA). In HSWA section 3004(o)(1)(A), EPA required all new landfills and surface impoundments to have double liners and leachate collection and removal systems. The purpose of a clay liner in a waste management facility is to serve as a barrier between waste materials and the hydrogeologic environment by limiting seepage from the facility and to provide support for overlying components of the facility. EPA has proposed a minimum hydraulic conductivity of 1×10^{-7} cm/s for the bottom liner material used in landfill design and construction.

Selection of a liner material that can be compacted to the required permeability involves a series of laboratory tests of the engineering properties of the materials. In addition to meeting permeability requirements, the liner material must be compatible with the waste that it would be expected to contain, because, depending on the nature and reactivity of the leachate, different physical and chemical reactions occur. These reactions may cause changes in the properties of the liner materials which may ultimately affect the performance of the liner. In order to safely contain hazardous waste in a landfill, knowledge of the physical and chemical processes involved must be attained.

A review of literature indicates that a wide variety of organic chemicals have

been landfilled in the past. There is, however, little available information concerning the impact of organic fluids, which form a major constituent of the leachate, on the properties of the liner material. Also, the effect of many chemicals and chemical mixtures on clay soils is not well understood. Some information may be obtained from a review of the research that has been carried out and qualitative statements can be made regarding the behaviour of certain clays in the presence of different types of fluids.

2.1.1 Classification of Hazardous Wastes

There are several widely accepted classifications of hazardous wastes according to different sources or characteristics of the wastes as follows:

- Nature of the source such as specific or non-specific
- Characteristics of the waste such as corrosivity, ignitability, toxicity, reactivity
- Hierarchy such as form or phase distribution, organic or inorganic, chemical class (solvents or heavy metals, treatability)
- Waste management methods such as on-site waste or off-site waste.

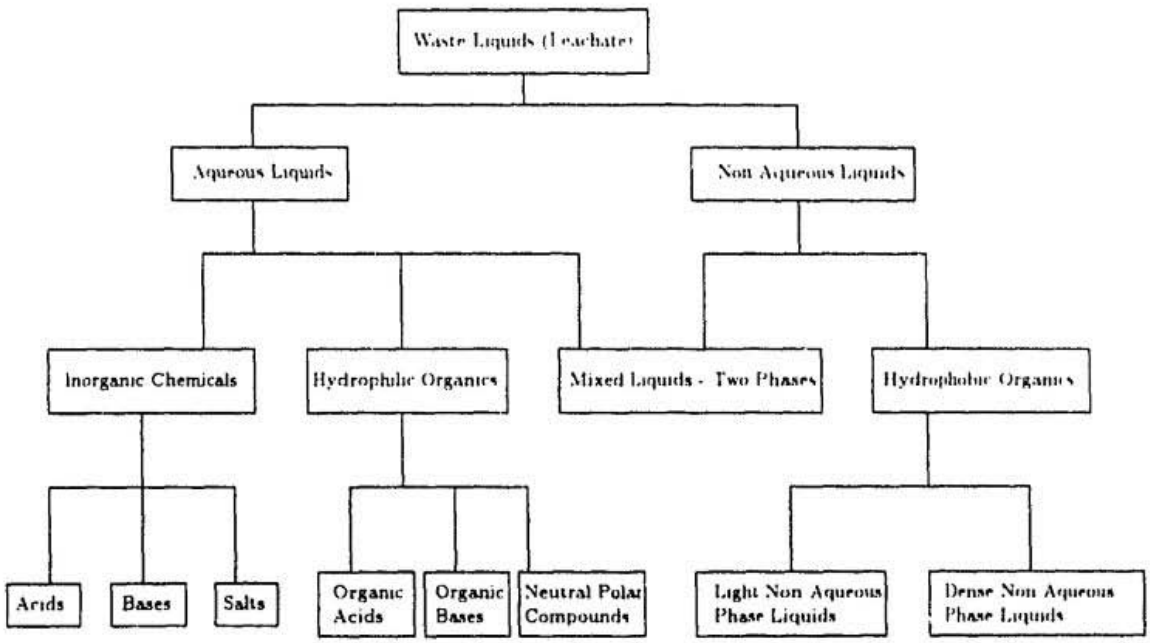


Figure 2.1: Hazardous Waste Classification (after Shackelford, 1994)

Perhaps, one of the most common methods of classification is that given by Shackelford (1994), as shown in Figure 2.1, according to the nature of the waste fluids.

2.2 Properties of Clays

Clay minerals are defined (Grim 1968) as

> "Microscopic phyllosilicate mineral particles of a colloid nature, laminated as layers of plates and having an effective diameter of < 0.002 mm"

This small effective diameter severely restricts ground water advection and limits intra-aggregate contaminant transport to mostly molecular diffusion, thus making clays effective liner materials. Clay minerals are hydrous phyllosilicates - largely of aluminium, magnesium and iron, that, on heating, lose adsorbed and constitutive water and yield refractory material at high temperatures. Clay minerals may be roughly categorized into four groups according to the basal distance of the unit cell, composition of the sheets and the kind of bonding that forms between unit layers. These groups are kaolinite, illite, smectite, and chlorite. The properties of only those clay minerals that were used in this study are reviewed in this section.

2.2.1 Kaolinite minerals

Kaolinite is a 1:1 layer non-expandable clay having a low cation exchange capacity, low specific surface area and a very low potential for shrink swell. The structure of kaolinite has been studied in detail by several investigators (Brindley and Robinson 1946; Bailey 1963) and is shown schematically in Figure 2.2. The structure is composed of a single silica tetrahedral sheet and a single alumina (Gibbsite) octahedral sheet combined in a unit so that the tips of the silica tetrahedral and one of the octahedral sheet form a common layer. In the layer common to the octahedral and tetrahedral groups, two-thirds of the atoms are shared by the silicon and aluminium. The mineral is triclinic. The layers are continuous in the a and b directions and are stacked above one another in the c direction (Grim 1968). The charges within the structural unit are balanced. The structural formula is $(OH)_8Si_4Al_4O_{10}$ and the theoretical composition expressed in oxides is $SiO_2 - 46.54\%$, $Al_2O_2 - 39.5\%$, $H_2O - 13.96\%$.

The unit cells are held together by van der Waals forces of attraction and hydrogen bonding between the tetrahedral and octahedral sheets of adjacent unit cells. These bonds are strong enough to preclude the introduction of water between the unit cells, thus preventing an interlayer swelling. The stacked crystal structure of kaolinite results in a blocky form for this clay mineral and a larger size and lower surface to volume ratio than other clay minerals. This low surface area,

combined with the relatively small negative surface charge, results in kaolinite being the least electrochemically active and least plastic clay mineral (Goldman et al. 1990). Ross and Kerr (1931) analyzed many samples of kaolinite minerals and concluded that lattice substitution was minimal. The variation between members of the kaolinite group is due to the difference in the stacking of sheet unit layers one above the other and in the position of the aluminium atoms in the octahedral layer. Kaolinite has a higher anion exchange capacity than most clay minerals. This may be due to the presence of replaceable hydroxyl ions on the outside of structural sheets.

Compared with other clay minerals, kaolinite has a lower affinity for water and a lower dispersivity and does not achieve a low permeability upon compaction. The permeability may be 2–5 orders of magnitude higher than that of smectitic clays and about 1–3 orders of magnitude higher than that of illitic clays. Since it is electrochemically inactive, its behaviour may be less affected by chemicals than other clay minerals. Thus, a kaolinitic clay liner may have a higher permeability than liners composed of other clays, but the permeability of a kaolinitic clay liner may not be as sensitive to changes in moisture content or chemical attack.

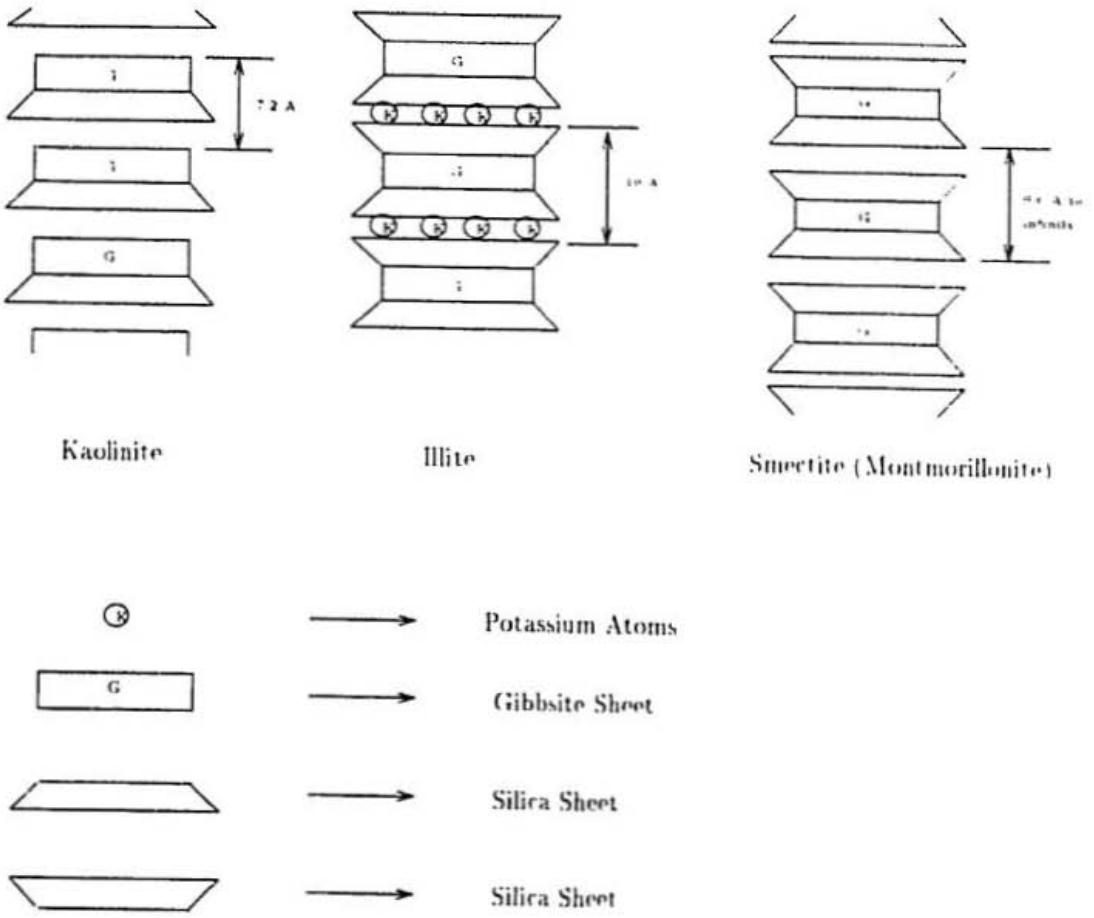


Figure 2.2: Schematic of Clay Mineral Structure (after Mitchell, 1976)

2.2.2 Illite minerals

These are defined as mica-like clay minerals because of their structural similarity to hydrous micas. A schematic diagram of the structure of illite is shown in Figure 2.2. Illites are composed of mica-like three-layer sheets with an octahedral (Gibbsite) sheet between two silica tetrahedral sheets (2:1 structure). These layers may be bound together by fixed or exchangeable cations (potassium for illite). The specific mineral species in this group are determined by differences in octahedral sheet composition and the type of interlayer cations. Two minerals in this group that occur commonly in soils are illite and vermiculite. Grim (1968) suggested that the illite clay minerals differ from well-crystallized micas in several ways including lesser substitution of Al^{3+} for Si^{4+}, randomness in the stacking of layers in the c direction, size of illite particles etc. The structural formula is $(OH)_4K_2(Si_6.Al_2)Al_4O_{20}$ and the theoretical composition is $K_2O - 11.8\%$, $SiO_2 - 45.2\%$, $Al_2O_3 - 38.5\%$ and $H_2O - 4.5\%$.

In terms of properties important to clay liner performance, illite lies between the kaolinite and smectite clay minerals. It should be noted that, although extensive isomorphous substitutions render a net negative charge on the clay surface, the fixed potassium ions in illite balance the charges and strongly bond the adjacent sheets together. As a result, illite has intermediate values for swelling index, activity, cation exchange capacity and also reaction to chemicals when compared

to kaolinite and smectite. The potassium ions effectively prevent the intercalation of water, organic liquids and other cations (Deer et al. 1966). Adsorption is largely confined to the external unit surface layers (Anderson et al. 1981).

2.2.3 Smectite minerals

Smectite is composed of units made up of silica sheets with a central octahedral (Gibbsite) sheet as shown schematically in Figure 2.2. The smectite minerals may be divided into two groups, based on the composition of the octahedral sheet. The montmorillonites have a dioctahedral, aluminium-based octahedral sheet, and the saponites have a trioctahedral magnesium-based octahedral sheet. Only montmorillonite, which is commonly found in soils, is discussed in this section. The theoretical formula without considering lattice substitutions is $(OH)_4Si_8Al_4O_{20}.nH_2O$ and the theoretical composition without the interlayer material is $SiO_2 - 67\%$, $Al_2O_3 - 28\%$ and $H_2O - 5\%$ (Grim 1968).

The outstanding feature of the smectite structure is that water and other polar molecules, such as certain organic molecules, can enter between the unit layers causing the lattice to expand in the c direction. The c axis dimension of smectite, is, therefore, not fixed. The bonding between the sheets is weak, and, as a result, the layers are easily separated by adsorption of water or other polar liquids. The loose bonding between the smectite layers results in a greater

capacity for volume changes. The interlayer spacing may vary from 9.6Å(1Å= 0.1μ) to complete separation, and this results in the high swelling behaviour and high activity of these clay minerals. Smectites have large cation exchange capacity due to a net negative charge arising from isomorphous substitutions. Due to the large negative charge, smectites can readily adsorb polar and positively charged organic species on interlayer surfaces. Exchangeable cations occur between the silicate layers and the c axis dimension also varies with the size and geometry of organic molecules that may be adsorbed. The expansion properties are reversible. However, when the structure is completely collapsed by the removal of all the interlayer polar molecules, re-expansion becomes very difficult.

Smectites swell readily in water due to hydration of interlayer cations and adsorption of multiple water layers on interlayer surfaces. A large degree of shrinkage can be expected when interlayer water is displaced by organic fluids because of the free swell of smectite in water. It is especially sensitive to alteration by chemical attack. Also, the type of cation occupying the interlayer spaces strongly influences the behaviour of smectite. The most commonly occuring interlayer cations are sodium and calcium. Limited swelling has been observed with calcium as the interlayer cation, whereas, when sodium is the interlayer cation, there is high swelling. Sometimes, the clay expands to 13.8 times its full volume when hydrated (Theng 1974).

Grim (1968) suggested that interlayer spacing in smectitic clays increases as dielectric constant and dipole moment of the adsorbed fluid increase. Since water has a high dielectric constant, most polar organics displacing water would tend to cause shrinkage due to decrease in interlayer spacing. If the total volume remains constant (no consolidation), the shrinkage of particles leads to an increase in the pore volume available for the flow of the organic liquid and may thus lead to an increase in permeability. Anderson et al. (1981) concluded that interlayer shrinkage, even just along large pore walls, could cause a significant increase in the permeability of a clay liner.

2.3 Clay - Chemical Interactions and Soil Permeability

Clay is the most important component of soil liners because the clay fraction of the soil ensures low hydraulic conductivity. However, researchers have found that clay liners typically used in landfills may be vulnerable to the effect of certain chemicals which can modify compacted clay soils of low permeability rendering them highly permeable. Goldman et al. (1990) suggest that changes in the permeability of clay soils due to chemical interactions may result from

- Alterations in soil fabric due to chemical influences on the diffuse double layer surrounding clay particles.
- Dissolution of soil constituents by strong acids or bases.
- Precipitation of solids in soil pores.
- Soil pore blockage due to the growth of microorganisms.

Any change in the water content of a clay mineral is likely to cause changes in the hydraulic conductivity of the material. This may be due to the displacement, extraction or replacement of water from the interlayer spaces by organic fluids. A combination of interlayer spacing decrease and particle rearrangement by organic fluids could cause changes in effective hydraulic pore diameter and affect the overall permeability of clay.

Griffin et al. (1976) evaluated the potential of clay minerals for attenuating the various chemical constituents of landfill leachate by passing leachate through laboratory columns containing mixtures of calcium saturated clays and washed quartz sand. They concluded that attenuation was a function of the Cation Exchange Capacity (CEC) of the clay mineral, the initial exchangeable cations on the clay, the chemical composition of the leachate and the pH of the leachate.

Pusch (1982) investigated the use of sodium bentonite as the active component of engineered barriers for disposal of radioactive wastes from nuclear reactors. He

suggests that sodium bentonite has a low permeability and ion diffusivity and also self-healing ability through swelling. These properties are attributed to mineral water interactions that yield a microstructural pattern with very narrow passages and a low average mobility of interparticle water molecules at high bulk densities.

A number of studies have established the importance of soil pore fluid electri cal characteristics in determining the engineering properties of fine-grained soils. Dielectric constant of the fluid seems to play an important role in causing changes in the hydraulic conductivity of clay soils. The effect of dielectric constant on the thickness of the double layer is given by (Mitchell 1976):

$$\frac{1}{H} = \left[\frac{\epsilon_0 DBT}{2n_0 e^2 \nu^2}\right]^{1/2} \tag{2.1}$$

where

H is the thickness of the diffuse double layer

ϵ_0 is the permittivity of vacuum (8.8542×10^{-12} (?^{2} J^{-1} m^{-1})

D is the dielectric constant of the medium

B is the Boltzmann constant (1.38×10^{-23} [J] [°K^{-1}])

T is the temperature [°K]

n_0 is the electrolyte concentration (ions/m^3)

e is the electronic charge (1.602×10^{-19} Coulomb)

ν is the cation valence

This relationship shows that, when other factors are held constant, the double layer thickness varies inversely with the valence and square root of concentration and directly with the square root of the dielectric constant and temperature.

Fernandez and Quigley (1985) conclude, on the basis of the Gouy-Chapman theory and microstructure analysis studies, that for a given void ratio, high permeability values are directly related to low dielectric constants of the pore fluid. Liquids having low dielectric constants are thought to cause double layer contraction during mixing, and formation of flocs or peds with huge macropores in between them. Dielectric constant and conductivity response were found to be influenced in a significant way by clay type and amount, water content, particle orientation as well as electrolyte type, amount and concentration.

Clay liner permeabilities are typically determined using relatively pure water as the leachate. In contrast, the actual leachates generated in industrial landfills are more likely to be either highly contaminated water or a mixture of organic and inorganic liquids released by the disposed waste (Anderson 1982). Where water is the permeant, several factors have been identified that strongly affect the permeability of clay-rich soils: grain size, fabric or arrangement of particles, degree of saturation, void ratio, electrolyte concentration, composition and nature of adsorbed cations and external pressure (Mitchell 1976).

Factors influencing the hydraulic conductivity of compacted clay include molding water content, degree of saturation, method of compaction, compactive effort, hydraulic gradient, size of clay clods, distribution of pore sizes, chemistry of permeant liquid, age of the test specimen, and void ratio (Boynton and Daniel 1985). Also, compacted clay soils often have permeability values lower than 10^{-8} cm/s, and it may be necessary to pass a pore volume of water through a soil before a stable baseline permeability value is obtained. After establishing the permeability baseline, the passage of at least a pore volume of organic test fluid may be necessary to fully determine the effects that the fluid may have on the permeability of the compacted soil.

In the case of clay-rich soils with aqueous fluids as permeants, the level of dissolved material is usually low and does not materially change the properties of the fluid from that of pure water. For permeation with organic fluids, the properties of the pore fluids, the chemical and mineralogical composition of the soil and the nature of the adsorption of the permeant by the soil particles are potentially important factors (Budhu et al. 1991).

Mitchell and Madsen (1987) list the most important factors that control the influences of organic chemicals on clay hydraulic conductivity. These include water solubility, dielectric constant, polarity of the organic liquid and whether the clay is exposed to the pure organic or a dilute solution. They suggest that

in almost all cases, pure organic liquids interact adversely with clays by causing some shrinkage and cracking, with concurrent large increases in hydraulic conductivity. Organics interact with clays by intercalation, adsorption on particle surfaces and ion exchange (Lagaly 1984). Intercalation involves the entry of organic molecules between silicate layers. Hydrophobic organics may also adsorb to the clay mineral surfaces. Adsorption of organic compounds on clay surfaces in aqueous systems depends on the available surface and the ability of the organic molecules to displace the water molecules (Mitchell 1976). Attraction of large organic molecules to clay surfaces by van der Waals forces may contribute to the total amount of organics held (Raussell-Colom and Serratosa 1987).

Fernandez and Quigley (1988) showed that water soluble organic liquids may dramatically increase the hydraulic conductivity of water saturated clayey soils, thus destroying their effectiveness as barriers for contaminants. Diffuse double layer contraction at constant void ratio was identified as a primary mechanism for such increases in hydraulic conductivity. However, they also found that the increased viscosity of solutions of some organics in water results in significant decreases in hydraulic conductivity. Budhu et al. (1991) conducted permeability tests using a consolidometer on kaolinite, montmorillonite and a clay-rich soil using a variety of organic fluids and water as permeants. They proposed an exponential equation that can be used to predict the permeability of soils for organic chemicals using the measured permeability for the soil with water.

Several investigators (Mesri and Olson 1971; Schramm 1981; Green et al. 1983; Brown et al. 1984; Gilligan and Clemence 1984; Anderson et al. 1985; Uppot and Stephenson 1989) have reported an increase in the permeability of clay rich soils when saturated with pure reagent grade organic fluid as compared to saturation with water.

Uppot and Stephenson (1989) studied the effect of acetic acid, aniline, methanol and xylene on magnesium montmorillonite and kaolinite. In the case of the montmorillonite, they found that methanol doubled the permeability and acetic acid tripled the permeability due to its reaction with the carbonates, liberating carbon dioxide. They report that aniline and xylene do not flow through saturated montmorillonite but flow through saturated kaolinite at reduced flow rates. They conclude that if the specimen is not saturated during permeation, then, immiscible fluids can permeate through the air voids in the specimen, thereby generating chemical reactions within the specimen.

Studies have also been undertaken to determine the threshold concentration below which organic chemicals do not alter the hydraulic conductivity of compacted clay and the results of the investigation showed that dilute organic chemicals (less than 80% by volume in an aqueous solution) have little effect on clay hydraulic conductivity (Brown et al. 1984; Acar et al. 1985; Bowders et al. 1986). Clearly, if the concentration of the waste liquid or leachate is maintained

below the threshold concentration, the liner material may well serve its purpose. It is, therefore, important to anticipate the kind and quality of leachate a site will generate and select the liner material accordingly.

Bowders et al. (1986) have evaluated the use of soil index tests to predict the potential for a leachate to react with a clay liner. The index tests investigated include Atterberg limits tests and sedimentation analyses. For acidic leachate, solubility tests have also been recommended. Such tests provide a simple, fast and economical means for preliminary screening of a leachate/soil combination to determine if there is significant potential for the leachate to affect the permeability of the liner.

2.4 Intrinsic Permeability Measurements

This section discusses the effect of various parameters such as, type of permeameter, backpressure saturation and hydraulic gradient on hydraulic conductivity measurements. Some of the criteria to be satisfied before the permeability tests can be terminated are also discussed in some detail.

2.4.1 Effect of Permeameter Type

Permeability cells also known as permeameters are used to evaluate the effects of waste-soil interactions on the hydraulic conductivity of soils. A variety of hydraulic conductivity cells are available for testing soils. Several studies have shown that large differences in measured hydraulic conductivity values can occur depending on the type of permeameter used in the test (Acar et al. 1985; Foreman and Daniel 1986). The permeability cells may be broadly classified into rigid wall cells and flexible wall cells.

The Rigid Wall Permeameter (RWP) is the simplest and most economical device available for lab testing of compacted clay samples. These permeameters consist of a rigid tube or box that contains the specimen to be permeated. The permeating liquid flows along the axis of the test specimen. The disadvantages of the RWP are that complete saturation of the void spaces in the clay sample is difficult, there is ordinarily no means of measuring the amount of shrinkage or swelling that might take place within the soil sample, and there is a potential for sidewall leakage (Bowders et al. 1986). Also, RWP may over-estimate the bulk hydraulic conductivity values whenever there is shrinkage and cracking of the specimen due to clay-chemical interactions. It is, however, very well suited for qualitative determination of whether or not adverse interactions exist between the clays and the selected chemicals. Research indicates that results from rigid

wall compaction mold cells compare well with results from field tests on prototype liners subjected to relatively low overburden pressure and permeated with concentrated organic solvents (Brown and Anderson 1983).

In the case of flexible wall permeameters (FWP), the test specimen is confined with porous disks and end caps on the top and bottom and by a flexible membrane on the sides. Undisturbed samples can be easily tested in FWP because minimal trimming is required and irregular surfaces can be easily accomodated. The chances of sidewall leakage are much reduced. Some disadvantages are a significantly higher cost than other types of permeameters, possibility of the flexible membrane being destroyed due to chemical reaction, and also diffusion of organic liquids through the membrane. Also, in contrast to the rigid wall type, FWP typically tend to underestimate the bulk hydraulic conductivity values. This may be due to the lateral confining pressure which prevents cracks from opening.

Foreman and Daniel (1984, 1986), using methanol as a permeant fluid in consolidation cell, flexible wall and compaction-mold permeameters, showed that the permeabilities in the compaction-mold devices were much higher than in the flexible wall device. The difference was attributed to sidewall leakage and a lower effective stress in the compaction-mold permeameters. Brunelle et al. (1987) studied the effect of permeameter type on hydraulic conductivity of a natural clay liner material using leachate from an active landfill. Comparative tests

were conducted using flexible wall permeameter, consolidation cell permeameter and double ring compaction-mold permeameters at a hydraulic gradient of 100. Again, permeabilities in the fixed wall permeameters were reported to be higher than in the flexible wall device. However, Boynton and Daniel (1985) who carried out the hydraulic conductivity tests on kaolinite and fire clay using the same three types of permeameters, reported that while hydraulic conductivity did vary from one permeameter to another, the type of permeameter did not have a large effect on the measured hydraulic conductivity.

2.4.2 Effect of Backpressure and Hydraulic Gradient

Slight deviations from full saturation have been shown to significantly affect measured permeability values (Mitchell et al. 1965). Backpressure can be used to help saturate the soil fully and to eliminate any gas that might tend to result in very low permeability values (Daniel et al. 1984).

The effect of applied hydraulic gradient and the associated stress levels on the measurement of the hydraulic conductivity of soils have been widely investigated (Olson and Daniel 1981; Boynton and Daniel 1985; Edil and Erickson 1985; Carpenter and Stephenson 1986). The effects of hydraulic gradient on the permeability of three clay soils to xylene and acetone was investigated by Brown et al. (1984). They conclude that hydraulic gradients of 31, 91, and 181 did not

greatly affect the permeabilities of either presaturated or unsaturated samples. Olson and Daniel (1981) found that excessively large hydraulic gradients may result in piping and migration of soil particles which may cause a decrease in hydraulic conductivity due to clogging of soil pores. Since relatively low hydraulic gradients are expected in the field, the effect of elevated hydraulic gradients in the laboratory is unconservative (Shackelford 1994).

2.4.3 Criteria for Concluding a Test

Clay-chemical compatibility testing should be continued until all changes in permeability resulting from the interaction of the chemical with the clay have been observed. To satisfy this condition, compatibility tests should be concluded only if the slope of the permeability versus time curve does not vary significantly from zero (steady-state permeability has been reached) and at least one pore volume of fluid has passed through the clay. In order to satisfy both the above conditions, it is necessary to determine the chemistry of both the influent and effluent and to report the number of pore volumes through samples as well as real time taken for flow (Goldman et al. 1990).

Chapter 3

Materials and Methods

A detailed account of the materials and experimental procedures used in this investigation is provided in this chapter, consisting of five sections. The first two sections introduce the clay materials selected in this study, the reasons for their selection and a listing of relevant physico-chemical properties. Section three describes the preliminary tests done in order to determine the index properties and physico-chemical properties of test clays. Equipment design and permeability testing procedures and calculations are discussed at length in the fourth section. The methodology used for Scanning Electron Microscopy (SEM) analysis of the microfabric of clays when exposed to test liquids is given in section five.

Table 3.1: Relevant Physical and Chemical Properties of Test Permeants

Test Liquid	MW	WS	VP	V	SG	DC	DM	ST
Acetic Acid	60.05	∞	11.8	1.16	1.05	6.16	1.74	28.80
Acetone	58.09	∞	184.8	0.34	.79	20.7	2.88	23.70
Aniline	93.13	36.0	0.4	4.4	1.02	6.89	1.53	42.90
Carbon Tetrachloride	153.81	34.0	90.0	0.97	1.59	2.24	0.0	26.95
Methanol	32.05	∞	96.0	0.55	0.796	32.63	1.7	22.61
Trichloroethylene	131.38	0.001	60.0	0.61	1.47	3.42	0.81	-
Xylene	106.18	0.2	10.0	0.81	0.87	2.27	0.0	28.37
Water	18.0	-	1.0	0.89	0.998	80.4	1.89	72.75

Source: Weast, CRC Handbook of Chemistry and Physics, 1975

MW=Molecular weight (g), WS=Water Solubility (g/L), VP=Vapor Pressure (bar), V=Viscosity (cp), SG=Specific Gravity (g/cm^3), DC=Dielectric Constant, DM=Dipole Moment (debyes), ST=Surface Tension (dyn/cm)

3.1 Permeants Used

Seven organic permeants were used for conducting clay-leachate compatibility testing with respect to changes in hydraulic properties and microstructure of selected clay minerals. These fluids may be broadly categorized into acidic, basic, neutral polar and neutral nonpolar types of fluids. Table 3.1 gives a listing of

relevant standard physical and chemical properties of the test fluids (Weast 1975). The reference permeant was distilled water. Previous studies (Anderson et al. 1981) have found distilled water to be compatible with test soils and also, it does not cause any significant change in the chemical make-up of clay.

Acetic acid is a carboxylic acid, and aniline is an aromatic amine that represents organic bases. Two different neutral polar liquids were selected - methanol is a neutral polar alcohol while acetone is a neutral polar ketone. Neutral nonpolar fluids selected include xylene, an alkyl benzene and chlorinated hydrocarbons, carbon tetrachloride (CTC) and trichloroethylene (TCE). All the permeants selected are fluid at room temperature. Acetic acid, methanol and acetone are infinitely soluble in water. Carbon tetrachloride and aniline are sparingly soluble in water while trichloroethylene and xylene are almost immiscible with water. These permeants were chosen because they are representative of fluids having a wide range of dielectric constants and aqueous solubilities, and are common constituents of leachate from hazardous waste landfills.

3.2 Clay Material

3.2.1 Origin and Type of Clays Studied

Three types of clays, viz. kaolinite, illite and smectite were used in this investigation. They are referred to as kaolinite, illite and smectite according to their major constituent.

Typical kaolinite has been described in section 2.2.1. It is stable when exposed to acids or high temperature environments (550°C) as compared to smectite which collapses under such conditions. The kaolinite used in this study was obtained from Hamill Gillespie, Port Newark, New Jersey.

Illite has intermediate shrink-swell behavior as compared to smectite or kaolinite (see section 2.2.2). The illitic clay used in the study was obtained from Canada Brick, Ontario.

Smectite clays have been introduced in section 2.2.3. The smectite investigated in this study is predominantly sodium bentonite. It was obtained commercially from Canada Clay Products, Saskatchewan. Sodium bentonite has been found to reduce the rate of contaminant migration by lowering the hydraulic conductivity and increasing the retardation factor. The clays were chosen to represent extremes in clay structure and properties. Though kaolinite and illite are

not used in pure grade as liner materials, several researchers have investigated the behaviour of these clays in laboratory studies and these materials were selected to provide a basis for comparison of results with those obtained in previous investigations.

3.2.2 Basic Characterization of Clays

This section gives a brief description of the preliminary testing methods employed to characterize the clays based on index and physico-chemical properties. The following tests were performed:

- Particle size analysis
- Specific gravity determination
- Atterberg limits tests
- Compaction tests
- Mineralogy X-Ray Diffraction studies
- Chemical tests pH and Cation Exchange Capacity

Table 3.2: Physical Properties of Clay Soils Studied

Clay Soil Description	Kaolinite	Illite	Smectite
Color (Dry Powder)	White	Gray	Grayish Brown
Mineralogy (From X-Ray)	90% kaolinite	40% illite	88% smectite
Specific Gravity (ASTM, D 854-83)	2.49	2.94	2.66
Liquid Limit (CAN/BNQ 2501-092)	60	31	141
Plastic Limit (ASTM, D 424-59)	33	19	40
Plasticity Index	27	12	101
Shrinkage Limit (ASTM, D 427-83)	31	19	32
Standard Proctor Test (ASTM, 698-70)			
Optimum Water Content (% dry weight)	25.5	14.5	59.0
Maximum Dry Density (g/cm^3)	1.66	1.88	0.99

Table 3.3: Chemical Properties of Clay Soils Studied

Clay Soil Description	Kaolinite	Illite	Smectite
Cation Exchange Capacity (meq/100g)	3.81	22.1	68.3
Exchangeable Cations (meq/100g)			
Sodium	1.6	1.7	36.7
Potassium	0.5	1.6	2.2
Calcium	1.1	16.3	24.0
Magnesium	0.6	2.5	5.4
pH (1:10 soil-water)	4.7	9.0	7.8
Carbonate Content (%)	0	2.0	0

Particle Size Analysis

The hydrometer test described in ASTM, D 422 - 63 was used for the determination of the distribution of particle sizes in the test clays. The distribution of particle sizes smaller than $2\mu m$ is determined by a sedimentation process using a hydrometer and the results are plotted in Appendix A.

Specific Gravity Determination

Specific gravity of test clays was determined using the pycnometer test method listed in ASTM, D 854 - 83. The values are given in Table 3.2.

Atterberg Limits

The procedures described in CAN/BNQ 2501-092 were followed for liquid limit and plastic limit determination. Plasticity Index, in percentage, is calculated as the difference between the liquid and plastic limits of clays. Table 3.2 gives the values of the Atterberg limits for each of the test clays and relevant plots are included in Appendix B.

For shrinkage limit determination, the mercury displacement method outlined in ASTM, D 427-83 was followed. The shrinkage limit values obtained for the

three clays are listed in Table 3.2.

Compaction Tests

The optimum water content used for computing maximum dry density of clays when subjected to a given compactive effort was determined for the three clays according to ASTM, D 698 - 70. Figures showing the resulting moisture content - dry density relationships of the three clays are included in Appendix C.

X-Ray Diffraction Studies

An X-Ray Diffractometer using the Rigaku Software was used to perform the X-Ray Diffraction experiments required in this study. The following scan conditions were employed:

Scan speed	=	5°/min
Radiation	=	Cu α
Scan angle (2θ)	=	3°-36° for untreated samples
		3°-18° for treated samples

A detailed description of sample preparation methods and relevant diffractograms are given in Appendix D.

Chemical Tests

- pH of clay soil suspension: 1:10 soil water ratio method was employed for determining the pH of the clay soils. A suspension of 2 g of clay in 20 ml of distilled water was shaken for 60 minutes in a reciprocating shaker and the pH of the suspension was measured. The values are listed in Table 3.3.

- Cation Exchange Capacity of Clays: Cation Exchange Capacity of the clays was determined using the ammonium acetate method. Samples were prepared in duplicate to ensure reproducibility of results. A detailed description of the test procedure is documented in Appendix E.

3.3 Procedures for Clay-Fluid Interaction Tests

3.3.1 Sedimentation Tests

The methodology followed by Bowders and Daniel (1987) for sedimentation analysis was adopted in this investigation. Sedimentation tests consisted of allowing 50 g of each clay to settle in 500 ml of liquid under gravity only. The distance from the surface of the supernatant liquid to the settling interface was recorded at regular time intervals, and was plotted as a function of time. The tests were terminated after 120 minutes for all permeant liquids including water as this time

was sufficient to cause complete settling in most organic fluids.

3.3.2 Modified Liquid Limit and Shrinkage Limit Tests

Modified liquid limit tests were performed on the clays using the same procedures as for liquid limit determination, but with organic permeants instead of water. The liquid limit is, therefore, expressed as a fluid (permeant) content (mass of liquid/mass of dry clay). No attempt was made to determine the plastic limit with pure reagent grade liquids due to health safety considerations.

Modified shrinkage limit tests were performed on (1) water saturated specimen and (2) specimen saturated with water for 24 hours and then mixed with pure organic liquids. Procedures were as in ASTM, D 427-83 but using a multiple molding container that accomodated four specimens at the same time for comparison purposes.

3.4 Permeability Testing Procedures and Calculations

A rigid wall permeameter with axial loading capabilities (oedometer) was used in this investigation. Figure 3.1 is a sketch of the test set-up used for measuring the

permeabilities of the clays with the organic permeants and with distilled water. A sectional sketch of the permeameter cell is shown in Figure 3.2.

The permeameter cell consists of a teflon ring containing the clay specimen, 38.5 mm internal diameter. The ring itself is placed in a teflon assembly. Teflon O-rings were used to ensure water-tight seals between the ring and the top and bottom parts of the cell. Sliding rams allowed for controlling the axial deformation of the specimen and for applying an axial effective pressure. Filter paper was placed between the specimen and the porous stones in all test runs to ensure uniform hydraulic end conditions. The whole set up was mounted under a fume hood to minimize worker exposure and accidental spills due to leakage. All tubings used in the permeameter were of teflon to ensure that deterioration of the tubings does not take place due to contact with the organic liquids.

Compacted clay soil cores were prepared by mixing the clays with distilled water to the desired water content (at or above optimum moisture content) and storing for at least 24 hours to hydrate. In this way, it was ensured that the samples were fully saturated before mounting in the cells. Clay liners used in landfills are ordinarily compacted wet of the optimum water content and naturally are completely saturated with water before they come into contact with the waste liquids. This point was taken into consideration when preparing the clay specimens. The material was then directly compacted in the ring, using a

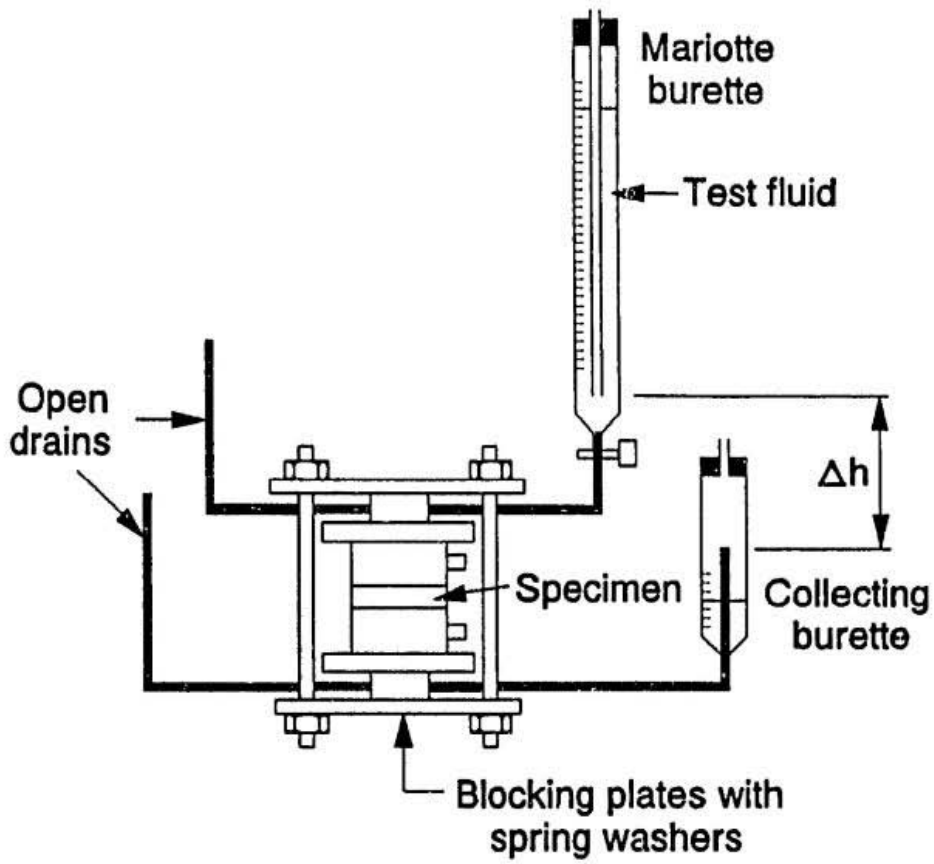


Figure 3.1: Test Set-Up for Permeability Studies

compaction assembly. No attempt was made to reach the maximum dry density. A standard kneading compaction method was used instead to produce specimens of uniform and repeatable density.

After compaction, the cores were mounted in the leachate cell and the permeants were allowed to pass through the samples. The compacted specimens were 10 mm in thickness and 38.5 mm in diameter. A Mariotte type graduated burette was used to provide the hydraulic head and liquid inflow. Effluent was collected from the fluid outlet to assess steady flow through the specimen. A graduate tube fitted with an air-tight cap to was used for effluent collection in order to prevent volatile losses. Typical duration of the test ranged from 15 to 22 days. Hydraulic gradients of 50 to 90 were used in these tests. For kaolinite and illite, at least five pore volumes of fluid were passed through each specimen before the test was terminated. In the case of smectite, the clay soil core was highly impermeable and in some instances, less than one pore volume of liquid was passed through the specimen over a period of 20 to 30 days. At the end of the tests, the samples were carefully removed from the cell and the dry density of each sample was determined and recorded. Data on water content, void ratio, degree of saturation, etc. of the test specimens are documented in Appendix F.

Constant head permeability tests were interpreted and used to compute hy-

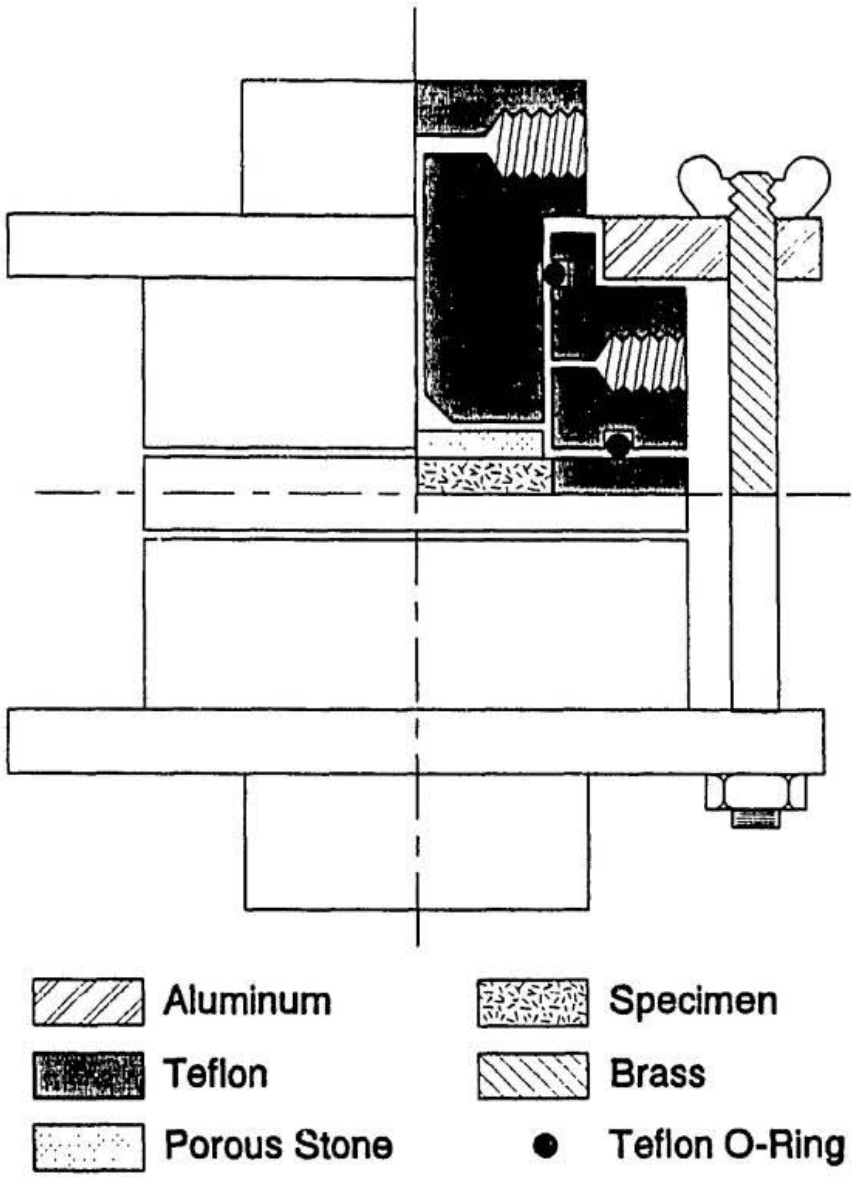


Figure 3.2: Sectional Sketch of Permeameter Cell

draulic conductivity as:

$$K = \frac{vl}{At\Delta h} \tag{3.1}$$

where

K	=	Hydraulic conductivity (cm/s)
v	=	Volume of permeant passed through the specimen (cm^3)
l	=	Length of specimen (cm)
A	=	Cross-sectional area of specimen (cm^2)
t	=	Time (s)
Δh	=	Hydraulic head difference (cm)

For the organic permeants, the value of K obtained by equation 3.1 is dependent on the viscosity and density of the permeant. In order to assess the changes in the clay structure itself, the specific or intrinsic permeability can be used. The intrinsic permeability is defined by (Freeze and Cherry 1979):

$$k = \frac{K\mu}{\rho g} \tag{3.2}$$

where

k	=	Intrinsic permeability (cm^2)
K	=	Hydraulic conductivity (Permeability when permeant is not water) (cm/s)
μ	=	Dynamic viscosity of test permeant (g/cm.s)

ρ = Density of test permeant (g/cm^3)

g = Gravitational constant (981 cm/s^2)

3.5 Scanning Electron Microscopy

The Scanning Electron Microscope (SEM) can be used to study the morphology of clay particles and their arrangements. Electron microscopy experiments require the use of an evacuated sample chamber, hence wet clays cannot be studied directly. SEM surfaces usually have to be coated with a conducting film to prevent surface charging and loss of resolution. Gold placed in a very thin layer in a vacuum evaporator is the conducting film used in this study. Several techniques are available for sample preparation. Some techniques studied include freeze drying, air drying and oven drying.

When possible, a Speedivac-Pearse Model 1 Freeze Dryer was used to freeze the samples which were then fractured and gold coated using a Edwards Model E12E Vacuum Coating Unit. However, in most instances, freeze drying was not practical (clay suspensions and specimens from shrinkage tests) and air drying followed by oven drying (110°C) was adopted. Fractured, gold-coated sections of the samples were examined using a Hitachi S570 Scanning Electron Microscope.

Accelerating voltages of 3, 5 and 20 KV were used in this study. Secondary electron images were recorded on Polaroid Type 665 Positive/Negative film. The microstructure of the clays in contact with different organic fluids was compared with the microstructure obtained with water under identical conditions. Photomicrographs which reveal the changes in the microstructure of the clays with the test permeants are presented in Chapter 4 and have all been obtained using oven-dried specimens.

Chapter 4

Results and Discussion

This chapter presents the major findings of this experimental study. The results of some preliminary tests such as sedimentation analyses and modified liquid limit tests are first discussed. On the basis of these results, an attempt is made to identify those types of liquids that may cause significant changes in the hydraulic conductivity and microstructural properties of clays. Permeability test results are discussed in detail for each clay with the test liquids. A visual indication of the changes in the microstructure of clays with organics as compared to water is provided through photomicrographs. A comparison of the results obtained in this investigation with the findings of past researchers is also presented in this chapter.

4.1 Sedimentation Tests

The results of the sedimentation tests are shown in Figure 4.1. All the nonpolar liquids caused the clay particles to flocculate rapidly and settle out of suspension within ten minutes, in the case of all the three clays. The flocs were large and visible. The same phenomenon was also observed in the case of polar acetone. The sedimentation rate in aniline was slower than in the nonpolar liquids, but faster than in methanol, acetic acid and water. The sedimentation velocities were much less in methanol than in other organic fluids. The sedimentation pattern of illite in acetic acid was quite different. There was rapid effervescence with release of a gas, presumably carbon dioxide and initial rate of settling was very low. In the case of water, there was no appreciable sedimentation for illite and smectite, within the test period of two hours. In kaolinite, almost complete settling was achieved in water, though at a much slower rate compared to the organics.

Settling velocity of spherical particles in liquids by gravity settling can be calculated using Stokes' Law given by (Mitchell 1976):

$$V = \frac{(\gamma_s - \gamma_w)d^2}{18\mu} \tag{4.1}$$

where

V = Settling velocity of spherical particles

γ_s = Unit weight of the particle

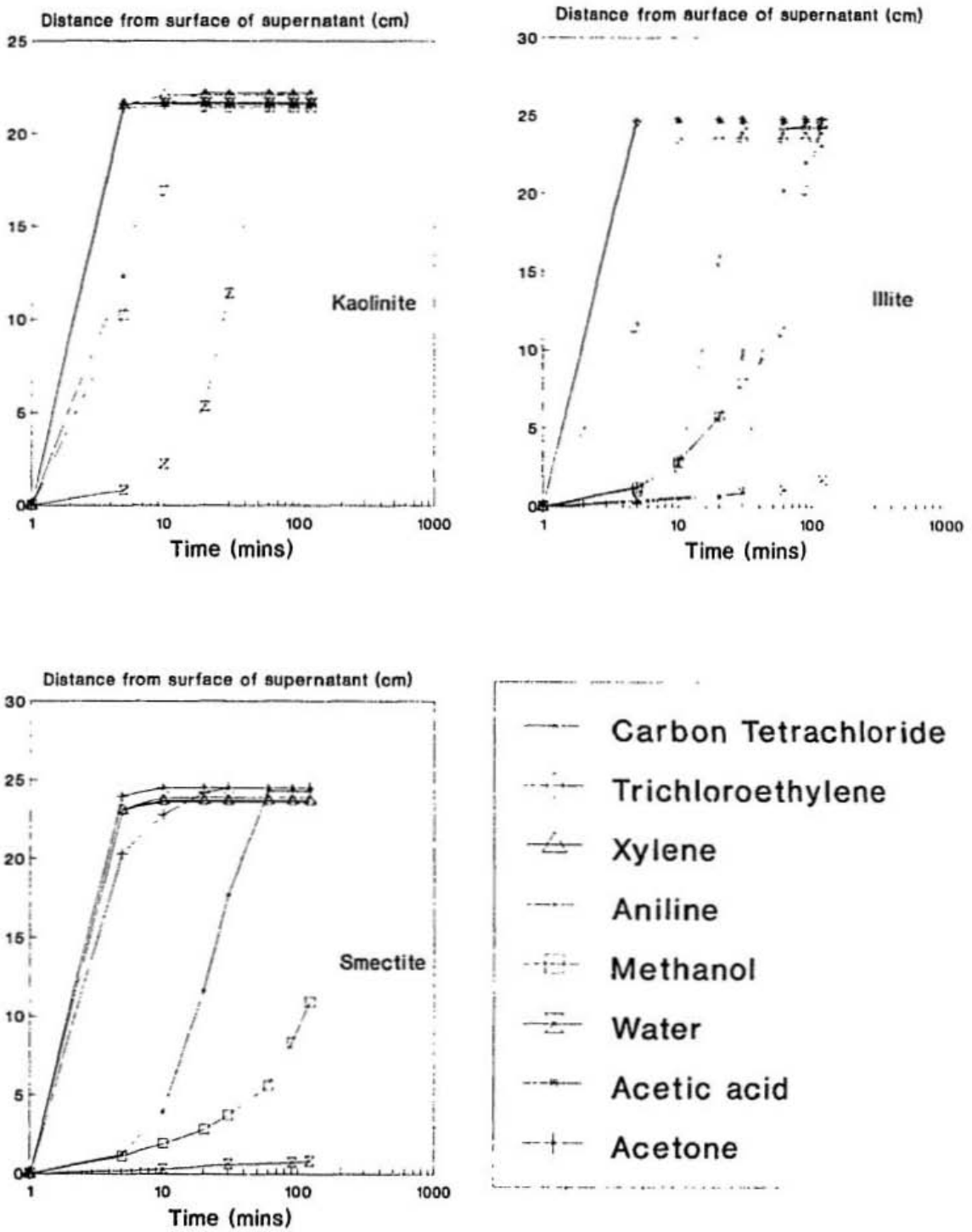
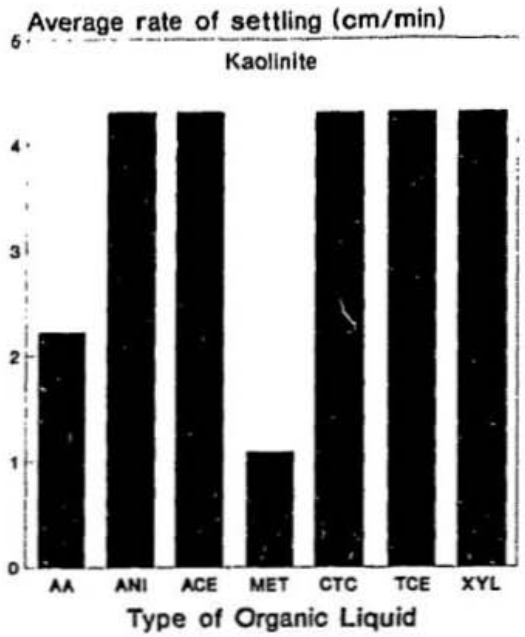
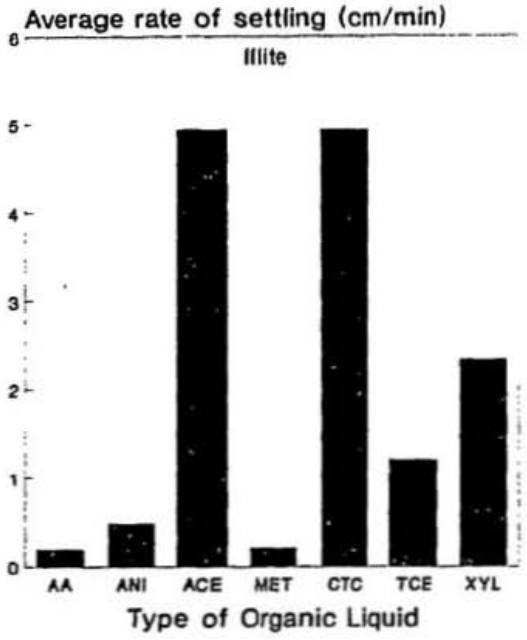
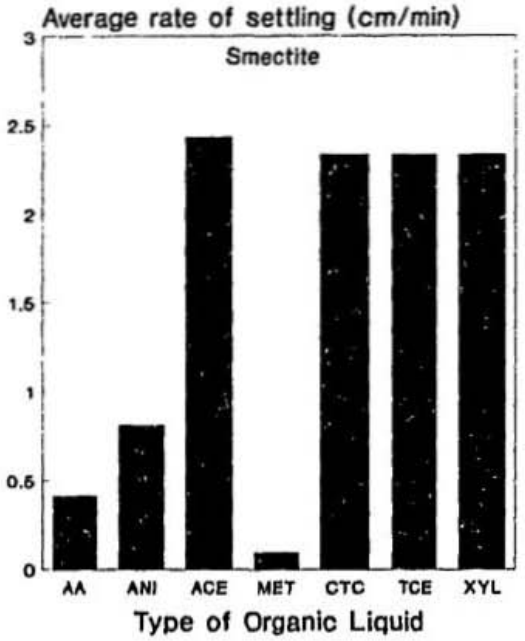


Figure 4.1: Sedimentation Test Profiles







AA - Acetic Acid
ANI - Aniline
ACE - Acetone
MET - Methanol
CTC - Carbon Tetrachloride
TCE - Trichloroethylene
XYL - Xylene

Figure 4.2: Rate of Settling of Clays in Organics

γ_w = Unit weight of the liquid

d = Diameter of the particle

μ = Viscosity of the liquid

The average rate of settling (cm/min) of the clay particles in each of the test liquids was computed from the sedimentation profiles as the ratio of the distance from the surface of the supernatant (cm) to the time taken for settling (min). Figure 4.2 shows the changes in the rate of settling in different liquids for each type of clay. Figure 4.3 provides for a comparison of results obtained with different clays for each organic liquid.

Dielectric constant of the permeant has been identified by some researchers as being a critical parameter affecting the hydraulic conductivity of clays (Green et al. 1981; Bowders et al. 1986). Trends observed in the sedimentation profiles also seem to point in this direction. Liquids having a very low dielectric constant cause almost instant flocculation of all the clays. It is seen that nonpolar liquids having a low dielectric constant collapse the diffuse double layer that surrounds the clay particles. The thin double layer promotes an edge-to-face orientation of the particles, which results in rapid flocculation of the particles. Flocculation of particles results in an increase in the effective diameter of particles. It is clear from equation 4.1 that, for a given type of soil particles, settling velocity increases with increase in particle size. The high rate of settling observed for acetone and

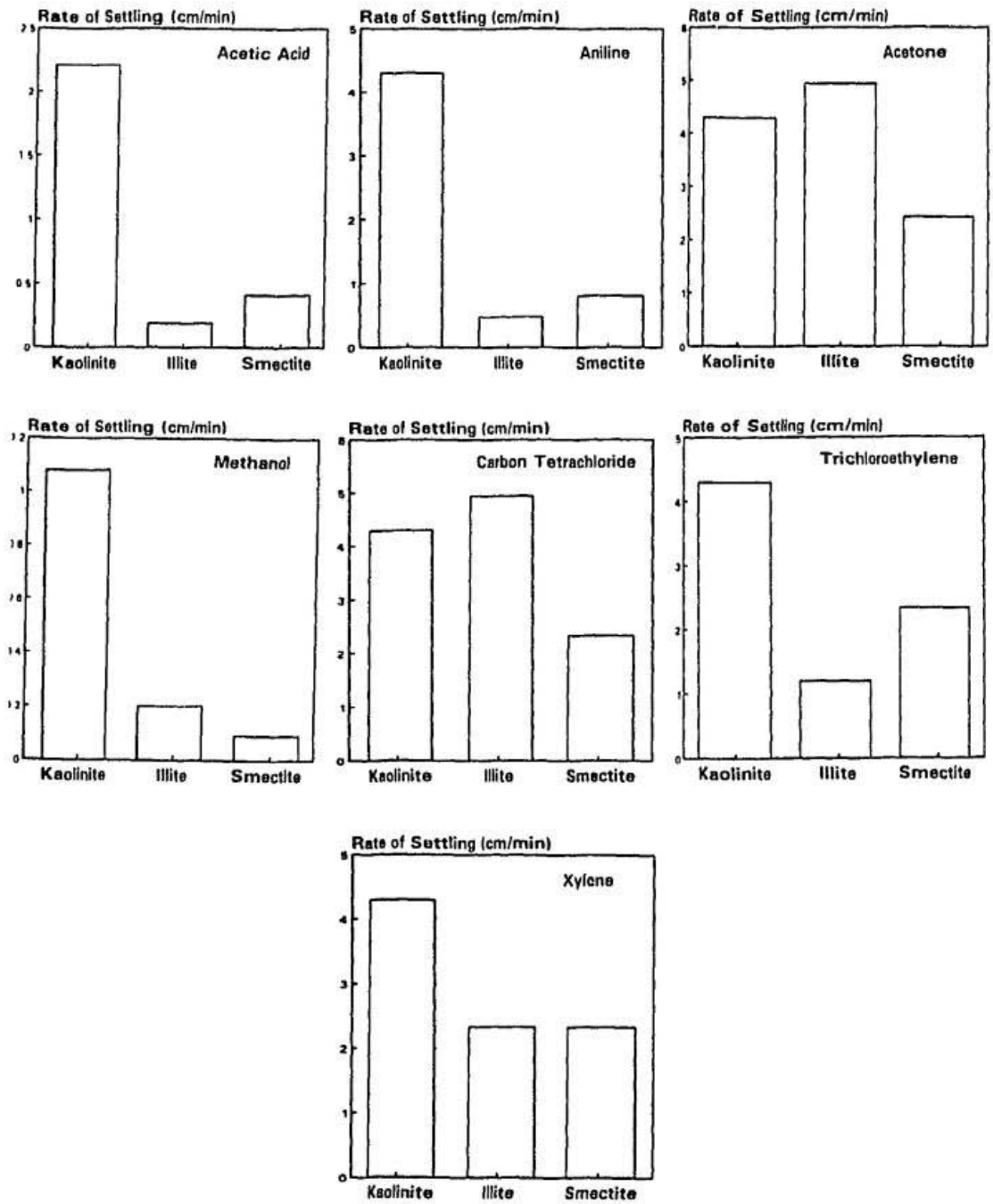


Figure 4.3: Comparison of Settling Rates of Clays

the nonpolar liquids in Figures 4.2 and 4.3 appears to be due to this reason. It is worth noting that acetone which has a dielectric constant of 20.7 also causes rapid settling. Since settling velocity is inversely proportional to the viscosity of the test liquid (equation 4.1), rapid settling in acetone is presumably due to the low viscosity of acetone. Inspite of its low dielectric constant, the rate of settling is observed to be much lesser in aniline than in acetone and the nonpolar liquids. This is thought to be due to the high viscosity of aniline. The relatively high dielectric constant of methanol results in lower sedimentation velocities for all clays. Kinematic viscosity, the ratio of viscosity to the density of a fluid, is thus an important parameter to be studied in conjunction with dielectric constant in the case of organic permeants.

Similar results have been reported by Bowders and Daniel (1987) for their soil index tests. A summary of relevant sedimentation results (qualitative) obtained by Bowders and Daniel for neutral compounds is given in Table 4.1, they observed that the weakly soluble compounds (heptane and TCE) do not cause flocculation of soil particles (kaolinite and illite-chlorite clays) when mixed with water at their solubility limits. However, rapid flocculation was observed in pure reagent-grade liquids. Based on the sedimentation profiles of kaolinite and illite-chlorite and the qualitative results listed in Table 4.1, they conclude that the effect of dielectric constant is unmistakeable. Mixtures with dielectric constant greater than 60 to 70 did not cause particles to flocculate. Brown and Anderson (1983) suggest that

Table 4.1: Summary of Relevant Sedimentation Test Results (Bowders and Daniel, 1987)

Compound	Dielectric Constant	Flocculation
Water	80	No
Methanol	34	Yes
Trichloroethylene	3	Yes
Heptane	2	Yes
Trichloroethylene*	80	No
Heptane*	80	No

* denotes liquid dissolved in water at solubility limit; TCE = 53 mg/L, Heptane = 1100 mg/L

in the case of compacted clay, flocculation or aggregation of particles occurs in the presence of organics, which leads to the formation of macropores and shrinkage cracks. To investigate this hypothesis, the microfabric of all the clays in the unsaturated state, when exposed to the test fluids, was studied using the SEM (section 4.4).

4.2 Modified Liquid Limit and Shrinkage Limit Tests

The results of the modified liquid limit tests are shown in Table 4.2. The liquid limit profiles are included in Appendix B. In the case of kaolinite and illite, there is over 100% increase in the liquid limit on permeation with the nonpolar fluids as well as the aromatic amine, aniline. There was no appreciable change in the liquid limit from the baseline values for water in the case of acetic acid, as well as the polar fluids, acetone and methanol. In the case of smectite, all the liquids produced a decrease in the liquid limit as compared to water, with acetic acid, acetone and methanol having almost identical values. When the clays were mixed with the nonpolar liquids, they became gritty and granular.

Normalized liquid limit is calculated as the ratio of the modified liquid limit obtained with organics to the baseline liquid limit obtained with water. The

Table 4.2: Results of Modified Liquid Limit Tests Using Various Organic Liquids

Liquid Type	Kaolinite	Illite	Smectite
Acetic Acid	55.9	31.0	58.2
Aniline	79.4	42.8	63.7
Acetone	61.1	32.5	58.2
Methanol	55.8	32.4	54.6
Carbon Tetrachloride	188.9	73.5	81.8
Trichloroethylene	166.5	67.2	74.5
Xylene	92.2	40.1	41.1
Distilled Water	60.5	31.5	140.9

normalized values are plotted for each of the clays over the entire range of organics tested in Figure 4.4. Results of Atterberg limits tests obtained by Bowders and Daniel (1987) for kaolinite and illite-chlorite clays are also plotted in Figure 4.4 for comparison. They observed that the liquid limit of illite-chlorite was not significantly altered by acid, which was also observed in the present study, for the illitic clay used. They also found that TCE and heptane strongly affected the Atterberg limits of both their test soils. Nonpolar liquids are found to cause large increases in the liquid limit of both kaolinite and illite in this study. All the organic liquids cause a decrease in the liquid limit in the case of smectite. Bowders and Daniel conclude that compounds with a dielectric constant greater than about 40 do not significantly alter Atterberg limits. It appears that a change in the thickness of the diffuse double layer, due to change in the dielectric constant of the test fluid, will cause a corresponding change in the liquid limit.

The results of the modified shrinkage limit tests are given in Table 4.3. Figure 4.5 shows a plot of normalized shrinkage limit for all the test liquids. Normalized shrinkage limit values were obtained with reference to the limit with water. Aniline appears to cause maximum increase in the shrinkage limit for all clays.

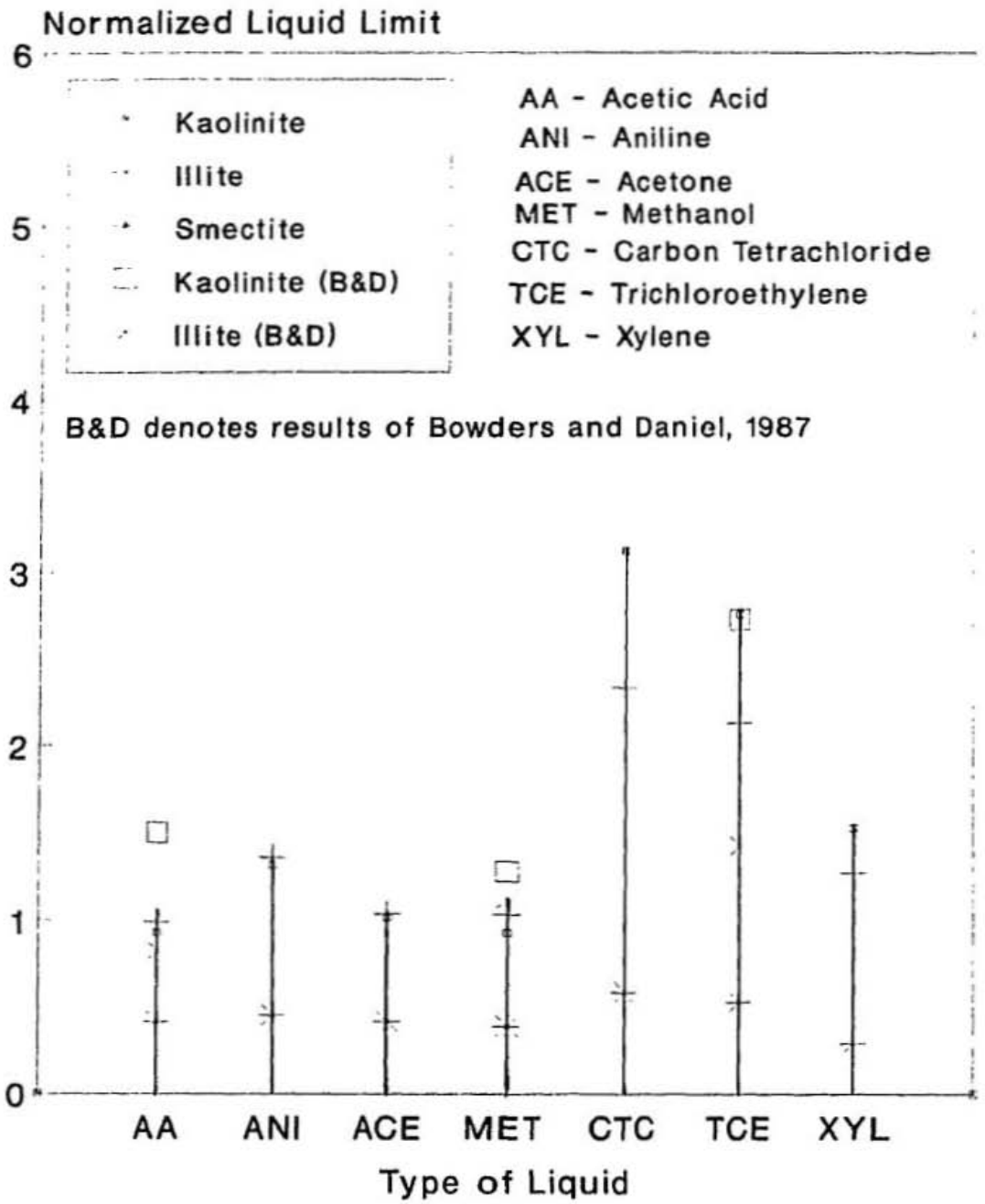


Figure 4.4: Comparison of Normalized Liquid Limits

Table 4.3: Results of Shrinkage Limit Tests

Liquid Type	Kaolinite	Illite	Smectite
Acetic Acid	30.8	17.6	39.6
Aniline	50.5	29.9	38.5
Acetone	33.7	16.3	27.6
Methanol	18.2	37.7	27.9
Carbon tetrachloride	36.2	23.7	34.6
Trichloroethylene	33.9	25.4	32.9
Xylene	37.0	20.5	37.3
Distilled Water	31.0	18.5	32.3

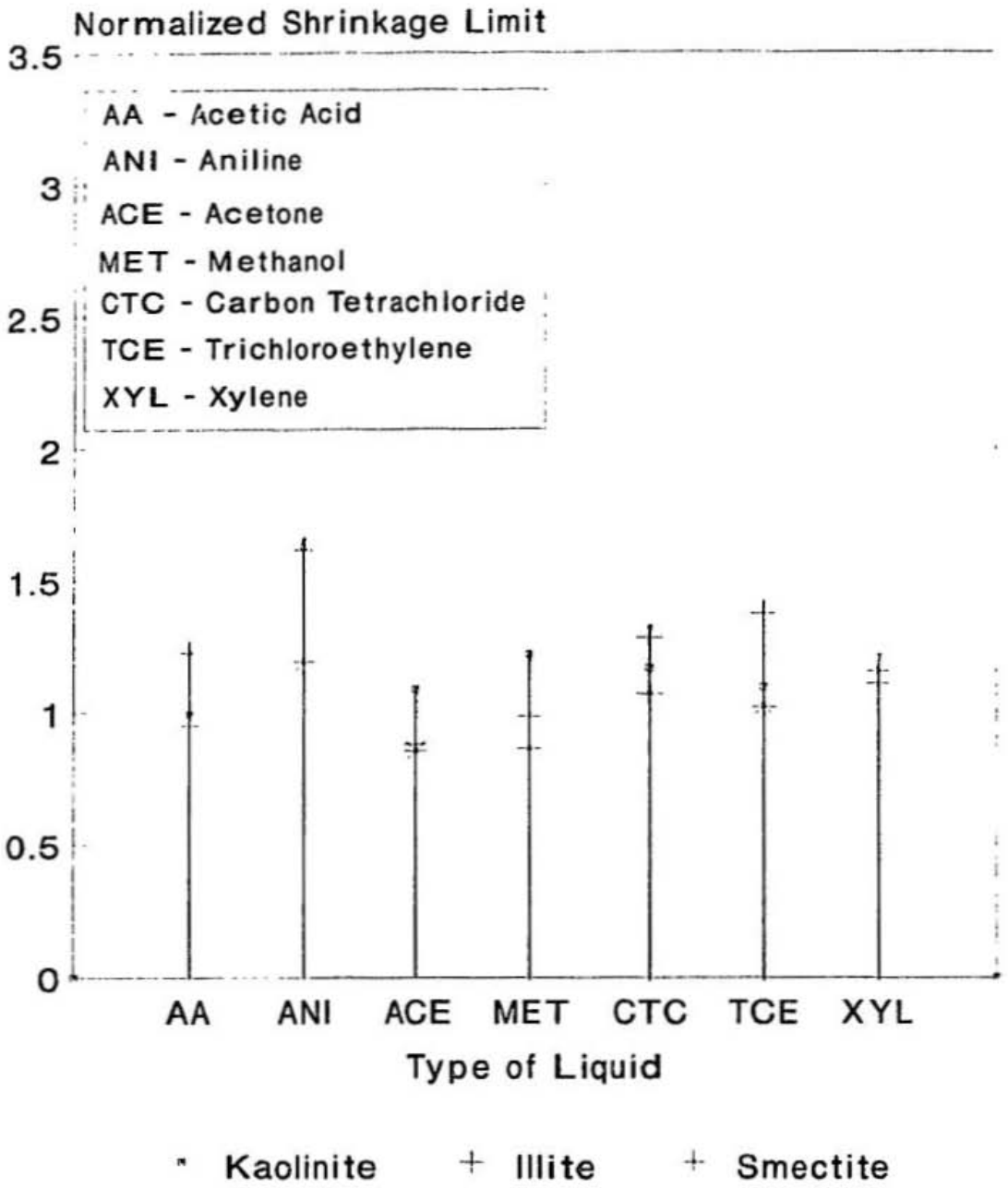


Figure 4.5: Comparison of Normalized Shrinkage Limits

4.3 Permeability Tests

4.3.1 General

The effects of the test permeants on each of the clays are discussed in the following sections. The test results consist of the records of the volumes of permeant passing through the specimen under a given total pressure head difference of Δh. From the raw data, a continuous curve has been fitted by eye and the rate of flow, Q(t), has been evaluated at discrete time intervals, t. Using Darcy's law (see section 3.4), the rate of flow has been converted into a hydraulic conductivity value, K, taking into account the dimensions of the test specimen (cross sectional area, A, and length, l) as follows:

$$K(t) = \frac{l}{\Delta h}\frac{Q(t)}{A} \tag{4.2}$$

The intrinsic permeability is then computed as:

$$k(t) = \frac{K(t)\mu}{\rho g} \tag{4.3}$$

The intrinsic permeability is recognized to be helpful in delineating the effects of the physical properties of the permeant (such as viscosity and density) from the properties of the porous medium itself. However, stating that k is dependent on the porous medium only would be oversimplified, because such a statement assumes that the specimen is fully saturated with the permeant and that the flow

channel distribution is not altered.

In the actual percolation experiments performed in this study, the clays were initially saturated with water and the organic fluid was introduced when a steady flow was obtained with water. Total substitution of pore water is, therefore, not likely to have been obtained, especially with immiscible liquids. Intrinsic permeability takes into account the viscosity-density effects of the test fluid, but does not consider the surface properties of the water/liquid/soil particles in the interface. When introducing the organic permeant, energy has to be spent in overcoming the resistance of separation of menisci between phases (in a way very similar to the desaturation of soils by air entry). Under constant pressure head difference, this can lead to either an increase or decrease in the flow rate, depending on the surface tension properties. In some instances, flow can even be stopped.

Also, chemical reactions between the clays and organic permeants can alter the pore size distribution and connectivity. Complex phenomena including clay surface complexation (internal or external), competition of organic molecules with water dipoles around adsorbed cations, substitution (exchange) of adsorbed ions in the electrical double layer around particles are among the processes that affect the flow capacity of clay materials. Moreover, these reactions depend on pressure, temperature and time and occur in a synergistic manner.

One type of approach may be to consider the hydraulic conductivity only, since it is directly related to the flow rate and allow for flux computations through liners, for instance. However, a more fundamental insight into physical and chemical interactions calls for the use of intrinsic permeability to eliminate, even imperfectly, some of the effects of the fluid physical properties. This approach has been preferred in the present study since emphasis is laid on changes in flow behavior.

Finally, the variability of specimen properties, primarily arising from preparation methods, must be taken into account. The values of the intrinsic permeability obtained have, therefore, been normalized using the initial k values obtained with distilled water in the first stage of each test. The intrinsic permeability with water ($(k_{water})_{initial}$), before percolating with organics, for each of the tests are given in Table 4.4. The permeability ratio, r_k (normalized intrinsic permeability, dimensionless) is defined as:

$$r_k = \frac{k_{permeant}}{(k_{water})_{initial}} \tag{4.4}$$

An r_k value greater than 1 means that an increase in permeability occurs when the saturation distilled water is replaced by another permeant. Raw data and intermediate plots, as well as physical characteristics of each specimen are given in Appendix E.

Table 4.4: Intrinsic Permeability Values with Water (cm^2) Before Percolation With Organics

Specimen tested before percolation with	Kaolinite	Illite	Smectite
Acetic Acid	1.1×10^{-12}	4.4×10^{-13}	6.8×10^{-14}
Aniline	1.6×10^{-12}	5.9×10^{-13}	6.3×10^{-14}
Acetone	1.6×10^{-12}	3.9×10^{-13}	20.3×10^{-14}
Methanol	1.2×10^{-12}	3.4×10^{-13}	7.3×10^{-14}
Carbon Tetrachloride	2.0×10^{-12}	10.0×10^{-13}	47.1×10^{-14}
Trichloroethylene	1.6×10^{-12}	10.2×10^{-13}	6.0×10^{-14}
Xylene	1.6×10^{-12}	5.4×10^{-13}	9.9×10^{-14}

4.3.2 Permeability Characteristics of the Kaolinite Clay

Figure 4.6 shows a plot of normalized intrinsic permeability of the kaolinite clay versus the number of pore volumes of flow of the test fluids . Six to fifteen pore volumes of permeant (water followed by organic liquid) were passed through the clay soil cores before the tests were terminated.

Acetic acid produced a slight decrease in permeability followed by a gradual increase to slightly over the baseline level. The final r_k value was 1.6, i.e. an increase in permeability of 1.6 times the baseline value with water. Anderson et al. (1985) report a decrease in hydraulic conductivity for kaolinite treated with acetic acid. They suggest that dissolution of iron oxides typically present in kaolinitic clays, followed by their migration into macropores may be the mechanism responsible for the observed decrease in k value. The subsequent increase in k may be due to soil piping which may have cleared or by-passed the clogged pores. Bowders and Daniel (1987) noticed a slight initial decrease in the hydraulic conductivity of kaolinite permeated with different concentrations of acetic acid. The decrease was less than one-half an order of magnitude.

Aniline caused an increase in the intrinsic permeability of kaolinite and the final r_k value was 3.8 upon passage of around ten pore volumes of the test liquid. Particle dissolution was not evident in the specimens at the end of the test. No visible cracks were detected. Aniline is a weak organic base and is sparingly solu

ble with water. Previous research work (Mitchell and Madsen 1987) suggests that aniline is too weak a base to cause dissolution of the clay particles. Hence, particle clogging due to dissolution cannot be a possible mechanism for the observed decrease in the permeability value. It appears that the predominant mechanism underlying the observed increase in permeability is the ability of aniline to modify the structural arrangement of the clay particles, at a microscopic as well as at a macroscopic level. This will be discussed in greater detail in section 4.4. In the studies conducted by Brown and Anderson (1983), aniline was observed to cause an increase in the permeability of various clays in a rigid wall permeameter. They did not observe evidence of dissolution or piping. They attributed the increase in permeability to alteration of the massive structure of the clays into an aggregated structure.

Neutral polar liquids, acetone and methanol produce a decrease followed by a slight increase in permeability values. The final normalized permeability values on termination of the tests were 0.8 and 0.6 for for acetone and methanol respectively. Displacement of interstitial water may be the mechanism for the observed decrease in permeability followed by the slight increase. Uppot and Stephenson (1989) observed only a slight trend towards an increase in conductivity for kaolinite with neutral polar fluids. Mesri and Olson (1971) suggest that when a fluid such as an alcohol is used as the test permeant, the fluid is adsorbed either by the cations or, more likely, by the formation of hydrogen bonds at the clay particle

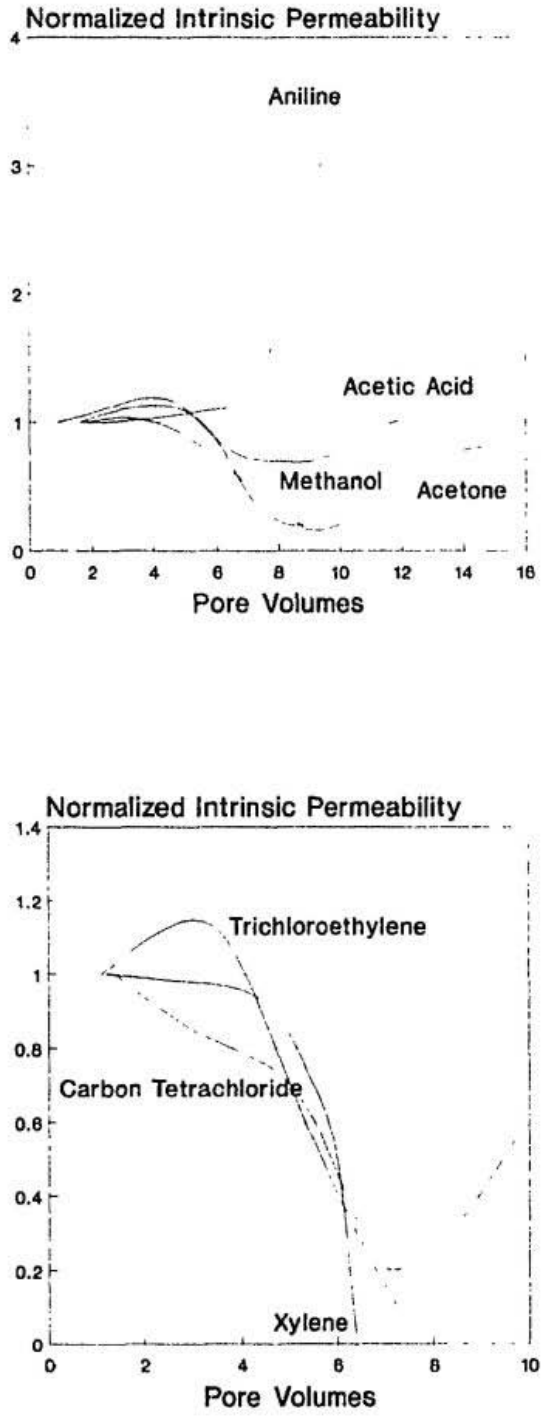


Figure 4.6: Permeability of Kaolinite to Test Liquids

surface, and a part of the flow channels is likely to be blocked, thus reducing the permeability. Anderson et al. (1985) observed that methanol-treated soils revealed development of large pores and cracks visible on the soil surface. They conclude that the dielectric constant of methanol may have caused a decrease in spacing between the clay minerals, thereby promoting structural changes.

The immiscible nonpolar liquids, trichloroethylene and xylene caused a marked decrease in permeability. The final normalized permeability ratio values were 0.03 and 0.01 for TCE and xylene respectively. The decrease in intrinsic permeability of around one order of magnitude as is seen in case of the immiscible fluids is a measure of the energy expended by these liquids in order to displace the interstitial water as the resident pore fluid. Similar results have been reported by Uppot and Stephenson (1989). They observed a decrease in permeability from 9×10^{-7} cm/s to 2×10^{-9} cm/s for kaolinite. Carbon tetrachloride shows a trend towards an increase in permeability after an initial drop. The final normalized permeability ratio was calculated to be 0.6 for CTC.

4.3.3 Permeability Characteristics of the Illite Clay

Changes in normalized intrinsic permeability of illite versus pore volumes of flow are plotted for all the test permeants and the results are shown in Figure 4.7. There was no visible formation of aggregates in the test specimen following per-

meation with water.

Acetic acid resulted in an initial decrease in intrinsic permeability. The figure shows a decrease followed by a trend towards an increase in k. Final r_k value for acetic acid was calculated as 0.5. Over four pore volumes of acid were passed before the test was terminated. Illite contains carbonate (2%) that may react with acetic acid resulting in the release of carbon dioxide. This gas appears in bubbles which cannot escape by dissolution in acid as would be the case in water. This may result in clogging or plugging of the pores. The observed decrease in k may be due to this phenomenon. Particle dissolution caused by the acid may also contribute to the observed decrease in k, since the dissolved particles may migrate within the macropores, thus blocking the fluid flow path. The subsequent trend towards an increase in intrinsic permeability upon passage of more pore volumes of acid may be due to occurence of soil piping. Anderson et al. (1985) conclude that any liquid capable of dissolving clay components (such as acids or bases) could potentially cause increases in the soil conductivity. Mitchell and Madsen (1987) suggest that the hydraulic conductivity of soils containing carbonates may decrease due to pore clogging by precipitates and particle migration.

An inital decrease in permeability followed by an increase is observed for aniline. Around six pore volumes of aniline were passed through the specimen before termination of the test. The final permeability ratio was 3.1. Since the

compacted clay specimens were saturated with water prior to permeation with aniline, the aniline had to physically replace water as the resident pore fluid. The initial decrease in permeability may be due to the energy expended by the aniline in displacing the interstitial water.

In the case of the neutral polar fluids, acetone caused a marked decrease in k value with the final permeability ratio being 0.04 when the test was terminated after passage of almost three pore volumes of acetone. Methanol caused a slight decrease followed by a slight increase in permeability. About seven pore volumes of liquid were passed before termination of the test and the final r_k value was around 0.9.

Two of the neutral nonpolar liquids studied in this investigation; trichloroethylene and xylene cause a decrease in the permeability of illite. The final permeability ratio values are 0.04 and 0.2 for TCE and xylene respectively. Over four pore volumes of liquid were passed through the specimen in the case of xylene and almost seven pore volumes of trichloroethylene were passed before the tests were terminated. Carbon tetrachloride, which is appreciably soluble in water, causes a slight decrease followed by an increase in the intrinsic permeability with a final k value of around 2.1. Around four pore volumes of liquid were passed through the specimen.

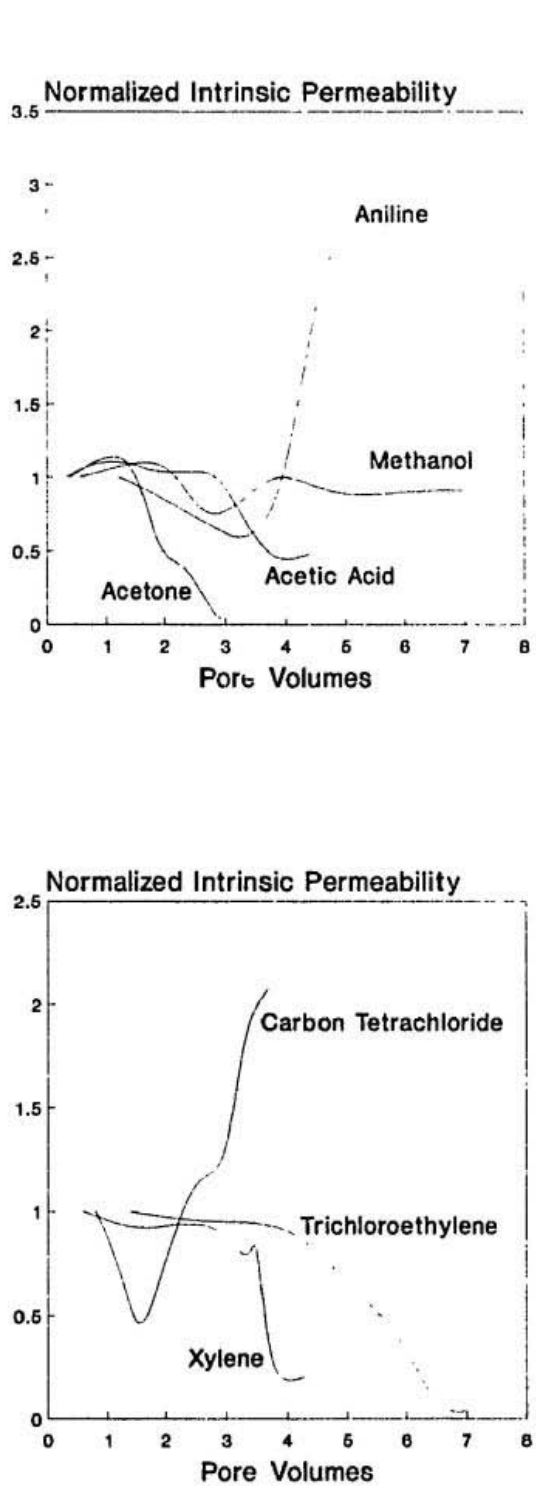


Figure 4.7: Permeability of Illite to Test Liquids

4.3.4 Permeability Characteristics of the Smectite Clay

The changes in the intrinsic permeability of the smectitic clay are plotted as r_k versus number of pore volumes of the test permeant in Figure 4.8. For the same duration, the number of pore volumes of test liquid that passed through the clay soil core, were much less for smectite than for the other two clays. This is because of the inherent low intrinsic permeability of the smectite.

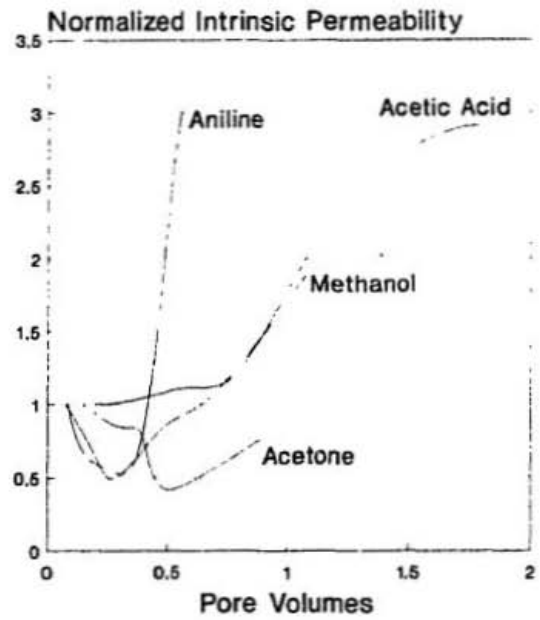
The smectite group of clays, especially montmorillonite, have been extensively studied by Theng (1974), with respect to the chemistry of clay-organic liquid interactions. In the present study, all the test liquids (with the notable exception of xylene) were observed to cause either an increase in permeability or a slight decrease followed by an increase over the baseline values. The primary mechanisms which affect the permeability profiles are thought to be the same as in the kaolinite and illite clays for each liquid.

The r_k value for acetic acid was 2.9. Around 1.7 pore volumes of distilled water followed by acetic acid were passed through the compacted smectite soil core. A gradual continuous increase in permeability is observed, which is presumably due to particle dissolution and migration. Aniline produced a slight decrease followed by a steep increase in permeability. The final normalized permeability ratio was computed to be 3.1. Around 0.5 pore volumes of permeant were passed before termination of the test.

Acetone and methanol both caused a slight decrease followed by an increase in the permeability. The final r_k values were 0.8 and 2.0 for acetone and methanol respectively. CTC and TCE both caused a continuous increase in permeability whereas xylene caused a decrease. Around 1.5 pore volumes of liquid were passed in the test with CTC and the final normalized permeability ratio was 2.5. Tests with TCE were terminated when about 0.5 pore volumes of flow had occured and the r_k value was 3.0. Around 0.6 pore volumes of distilled water followed by xylene were permeated and the final r_k value was 0.2.

4.3.5 Summary of Permeability Test Results

The final values of r_k upon termination of the permeability tests are summarized in Table 4.5. The kaolinite clay used in this study is not a very reactive material. Its low surface area and Cation Exchange Capacity mitigate potential chemical reactions with organic permeants. The organic permeants basically compete with water dipoles either in the electric diffuse layer around existing cations or directly at the clay surface. Neutral nonpolar molecules with large molecular mass (TCE, xylene and to a lesser extent CTC) seem to complex with kaolinite on the exter nal surface, thereby reducing the pore channel radii and the permeability. The marked increase in permeability with aniline, on the other hand, appears to follow other mechanisms.



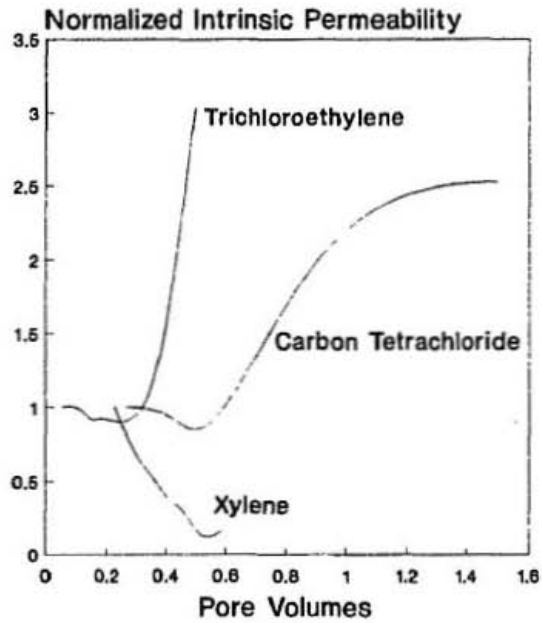


Figure 4.8: Permeability of Smectite to Test Liquids

Table 4.5: r_k Values at Termination of Permeability Tests

Liquid Type	Kaolinite	Illite	Smectite
Acetic Acid	1.6	0.5	2.9
Aniline	3.8	3.1	3.1
Acetone	0.8	0.04	0.8
Methanol	0.6	0.9	2.0
Carbon Tetrachloride	0.6	2.1	2.5
Trichloroethylene	0.01	0.04	3.0
Xylene	0.03	0.2	0.2

At the other extreme of clay behavior, smectite minerals are observed to have a high reactivity and exhibit marked changes when percolated with organic liquids. With the notable exception of xylene and to a lesser extent, acetone, the smectite clay hydraulic properties deteriorate with organic liquids by a factor of 2 to 3. It is, however, difficult to single out physical or chemical processes leading to these changes.

The illitic clay, as expected, lies in between these extremes with additional features due to its particular composition (presence of carbonate).

4.4 Microstructure Analysis

4.4.1 General

The previous sections have shown that the behavior of various clay minerals is affected by the composition of the pore liquid. Sedimentation tests demonstrated changes for clay suspensions, where individual interactions between fluid particle and particle-particle is the rule. The effective stress acting on the clay micropar ticles is limited to the self buoyant weight, and the structure can be described as flocculated (edge to edge contacts, honeycomb fragile structure, high void ratio and interconnectivity) or dispersed (edge to plane contacts, oriented anisotropic

structure, low void ratio and high tortuosity in the direction perpendicular to the particle orientation). Evidence of these loose structures is difficult to gather through microscopy studies because the drying process involves mechanical attraction forces that are likely to deeply deform the specimens. For suspensions or freshly deposited clays, the theoretical workframe of diffuse double layer and electrical potential appears to provide a qualitative explanation of the observed phenomena.

When studying the changes in index properties (physical or mechanical) such as liquid limit, plastic limit or shrinkage limit, the specimen is prepared from air dried clay material and mixed with the organic liquid using a high kneading energy. The combination of mechanical and electrical forces during preparation leads to a particular type of grouping of particles that can be described as domains, clusters and peds, with micropores and macropores (Yong and Sheeran 1973). At a microscopic level (magnification of at least $\times 1000 = 1$ K), domains (basic sets of particles) and clusters (sintering of domains) with the associated micropores constitute the observation units while peds, grains and macropores are characteristic of optical microscopy structure scale. In the following sections, an SEM magnification of 4 K has been selected to distinctly show single clay particles (diameter of the order of 1 μm) as well as clusters (diameter of the order of 4 to 10 μm) on a 70 $\times$ 95 mm photographic unit. The preparation of specimens for SEM studies involves fracturing of bits of dried clay and it was found that the

friability of specimens prepared with pure reagents prevented such a preparation and mounting. It was, therefore, decided to start from a water saturated clay paste (close to the liquid limit) that was mixed with sufficient amount of organic liquid (about 10% in volume) to ensure complete interaction between fluid and particles. These prepared mixes were used for the shrinkage limit determination tests and the oven-dried specimens were fractured and mounted for SEM examination. These photomicrographs are described and analyzed in sections 4.4.2 through 4.4.4.

In the study of changes in permeability following replacement of water by an organic permeant, the initial microstructure is obtained by heavy compaction in a mold, which obviously generates some variability in specimen void ratio. A correct microstructure analysis protocol would have been to

- duplicate specimens, keeping one as prepared and using the other for percolation with the fluid of interest.
- prepare and mount samples from both specimens for SEM ensuring that the microstructure is preserved.

The variability in initial void ratio combined with the size of specimen required for deep freezing and the corresponding structural damages that are unavoidable during SEM sample preparation as well as the need to obtain a dry weight of

the total specimen after percolation (for void ratio computations) lead us to put aside the microscopy analysis of specimens used in the permeability tests.

Furthermore, advective fluid transport through clay materials is controlled by the spatial size distribution and continuity of the flow channels. Changing the permeant is likely to affect the thickness of the adsorbed layer around particles and eventually, within the particles themselves (for smectite in particular). Since full reorganization of clay particles is not likely to be observed in a dense specimen (due to geometrical constraints), a change in permeability must be associated with a change in the effective flow channel size and availability (minimum opening). The present techniques available for sample preparation (dry) for SEM, it is probably impossible to observe such changes.

4.4.2 Microstructure of Remoulded Kaolinite Clay

The photomicrographs of the microstructure of kaolinite when treated with the test permeants are shown in Figures 4.9 and 4.10.

From the micrographs, it is observed that acetic acid, acetone and methanol do not cause significant alterations to the microfabric of kaolinite. There is no evidence of cluster formation or shrinkage or cracking of the fabric. Samples prepared with aniline, CTC, xylene and TCE show distinct clustering with large

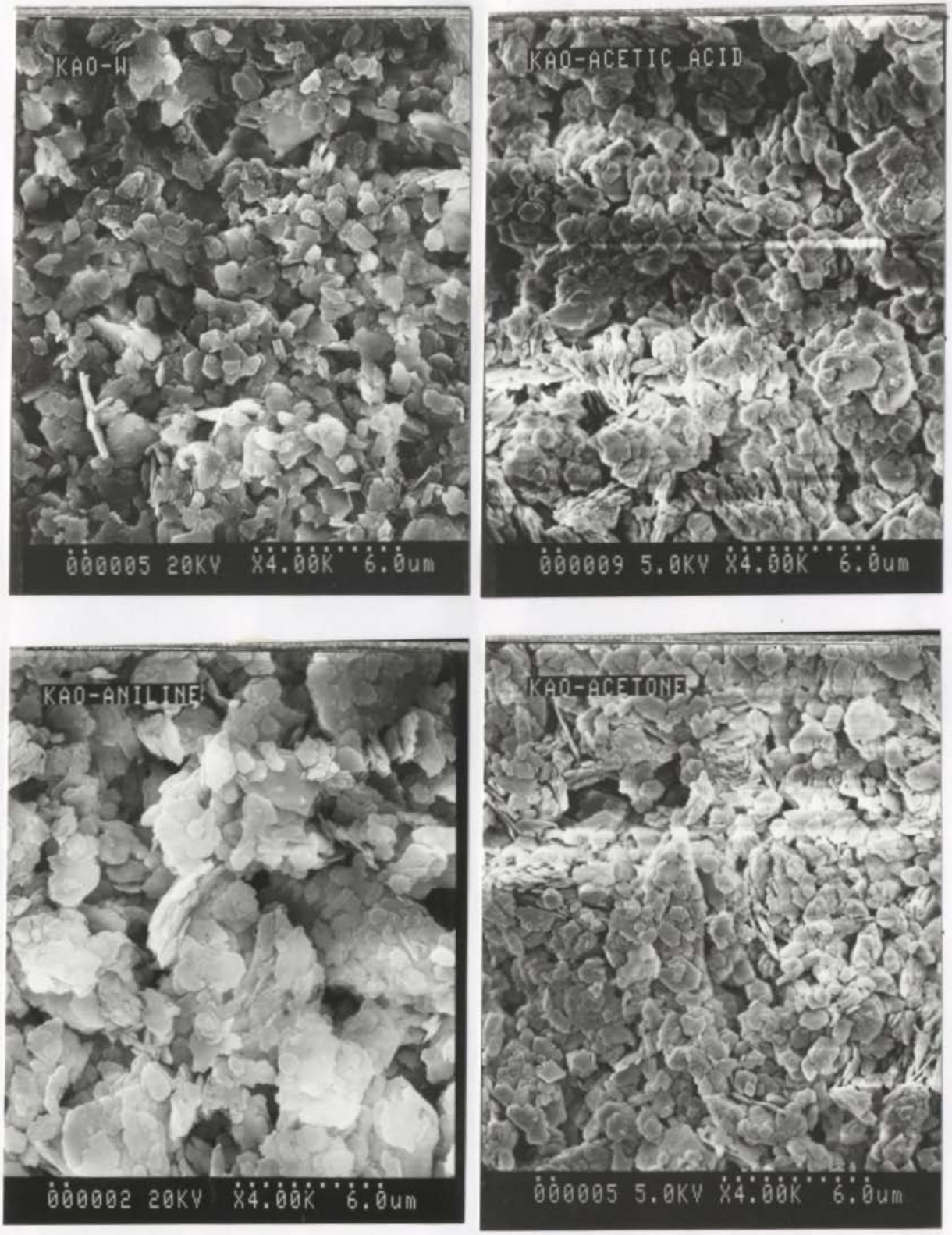


Figure 4.9: Photomicrographs of Kaolinite – (a) Water (b) Acetic acid (c) Aniline (d) Acetone

macropores. This is particularly true for aniline, where the surface reactions are such that the clay particles agglomerate when mixed with the organic fluid. The increased effective size of these clusters creates larger micropores when kneading action is provided. TCE and xylene have a similar influence on the grouping of particles. For CTC, the photomicrograph also indicates clustering in a manner that resembles fusion of domains rather than simple piling. No plausible explanation has been found for this case. It is worth noting that liquids which do not change the liquid limit significantly from the baseline values for water, such as acetic acid, acetone and methanol, do not cause significant alteration in the microfabric as well. Nonpolar liquids which cause over a 100% increase in the liquid limit appear to alter the microfabric to some extent.

4.4.3 Microstructure of Remoulded Illite Clay

Changes in the microfabric of illite prepared with different test liquids are shown in Figures 4.11 and 4.12.

Domain aggregation is observed for all organic liquids. The size of the cluster is particularly large for CTC and relatively small for aniline.

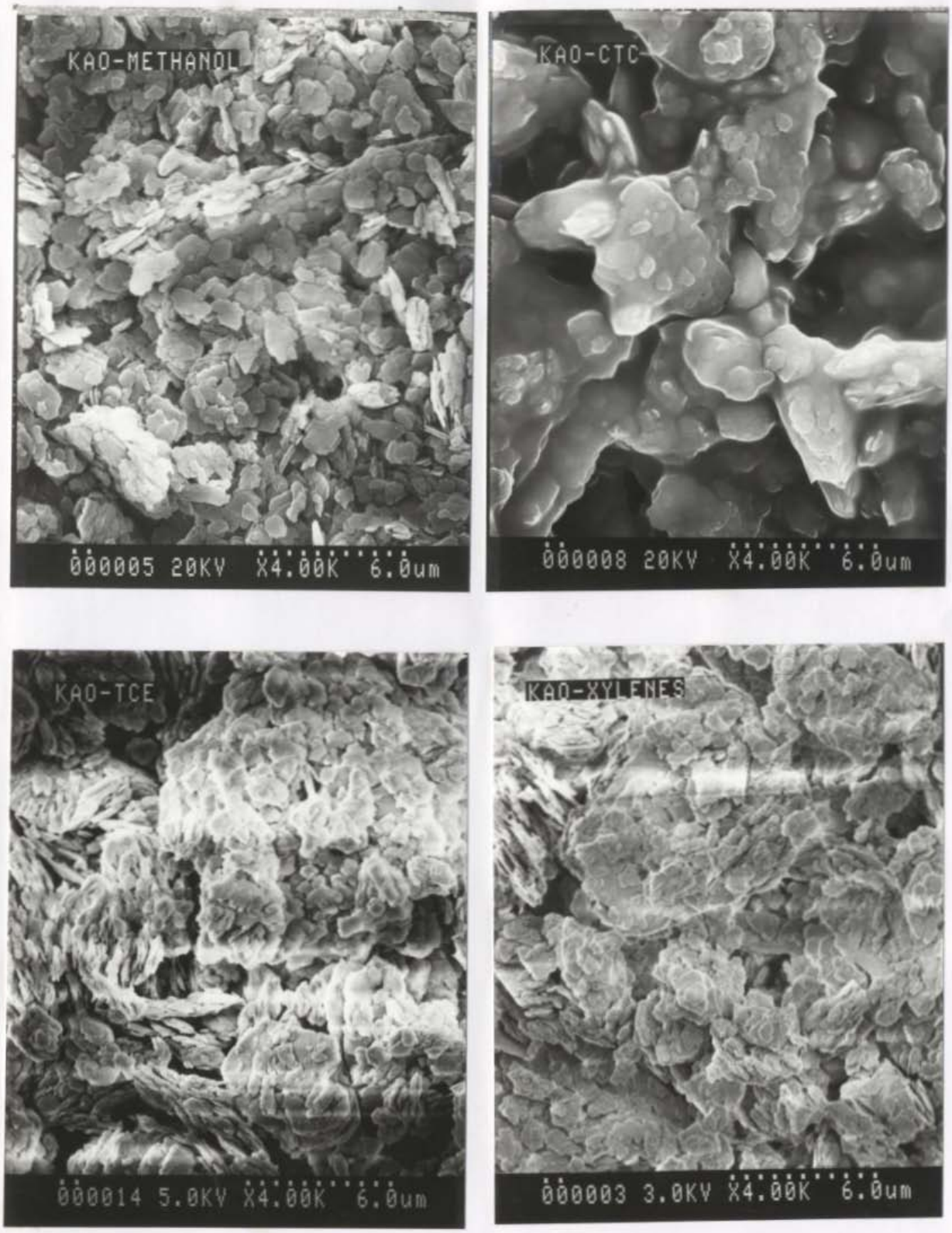


Figure 4.10: Photomicrographs of Kaolinite – (e) Methanol (f) CTC (g) TCE (h) Xylene

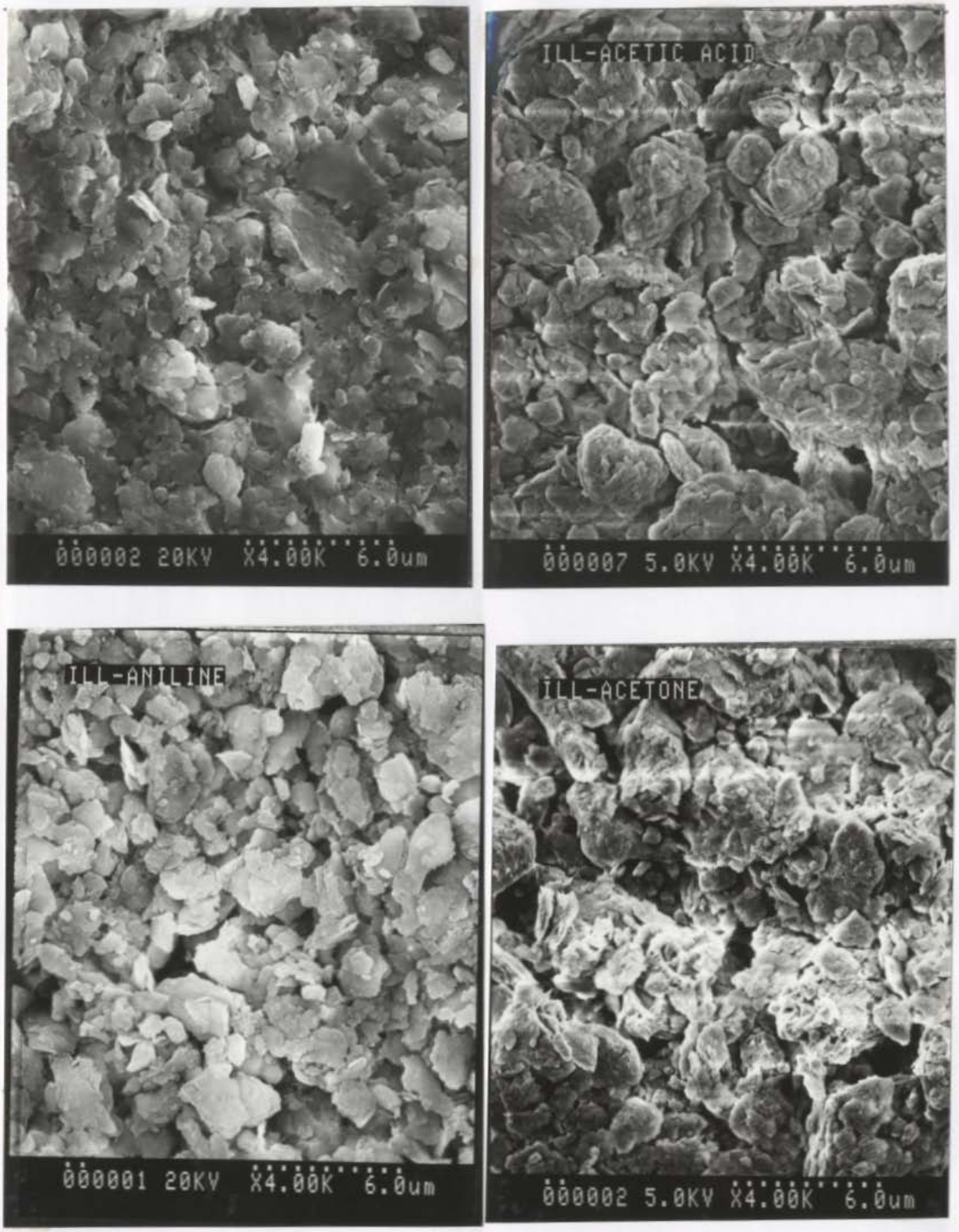


Figure 4.11: Photomicrographs of Illite – (a) Water (b) Acetic acid (c) Aniline (d) Acetone

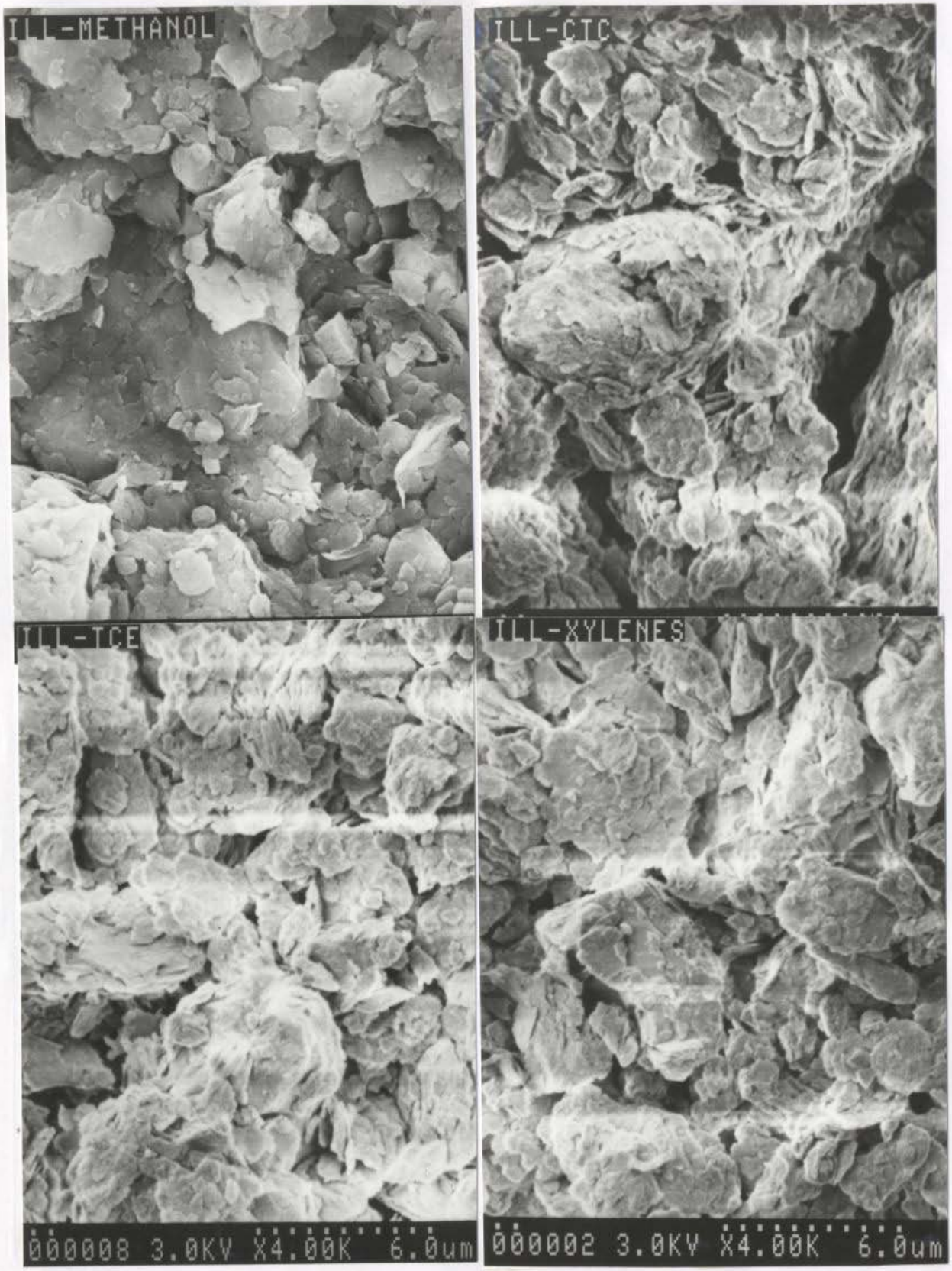


Figure 4.12: Photomicrographs of Illite – (e) Methanol (f) CTC (g) TCE (h) Xylene

4.4.4 Microstructure of Remoulded Smectite Clay

Photomicrographs of the microstructure of smectite when treated with the test permeants are shown in Figures 4.13 and 4.14. Considerable clustering occurs in the smectite clay when the water replacing organic liquid is aniline, methanol, CTC, TCE or xylene. For acetic acid and acetone, the initial (water saturated) structure is conserved within larger peds that are delineated by crack type voids. However, the latter features may be caused by the preparation process itself, which was more challenging for this clay. For the specimen treated with CTC, fusion of clusters seems to occur in a pattern very similar to the kaolinite clay specimen.

This formation of clusters can be associated with the rapid flocculation of the smectite particles in these liquids, as evident from the sedimentation tests. This is a visual indication of the double layer collapse due to reduction in the dielectric constant.

4.4.5 Summary of Microstructure Analysis Results

There seems to be a strong correlation between the results of the sedimentation and index property tests and the microstructure analysis. Maximum alteration in the microfabric seems to result from exposure to the nonpolar liquids. Immediate

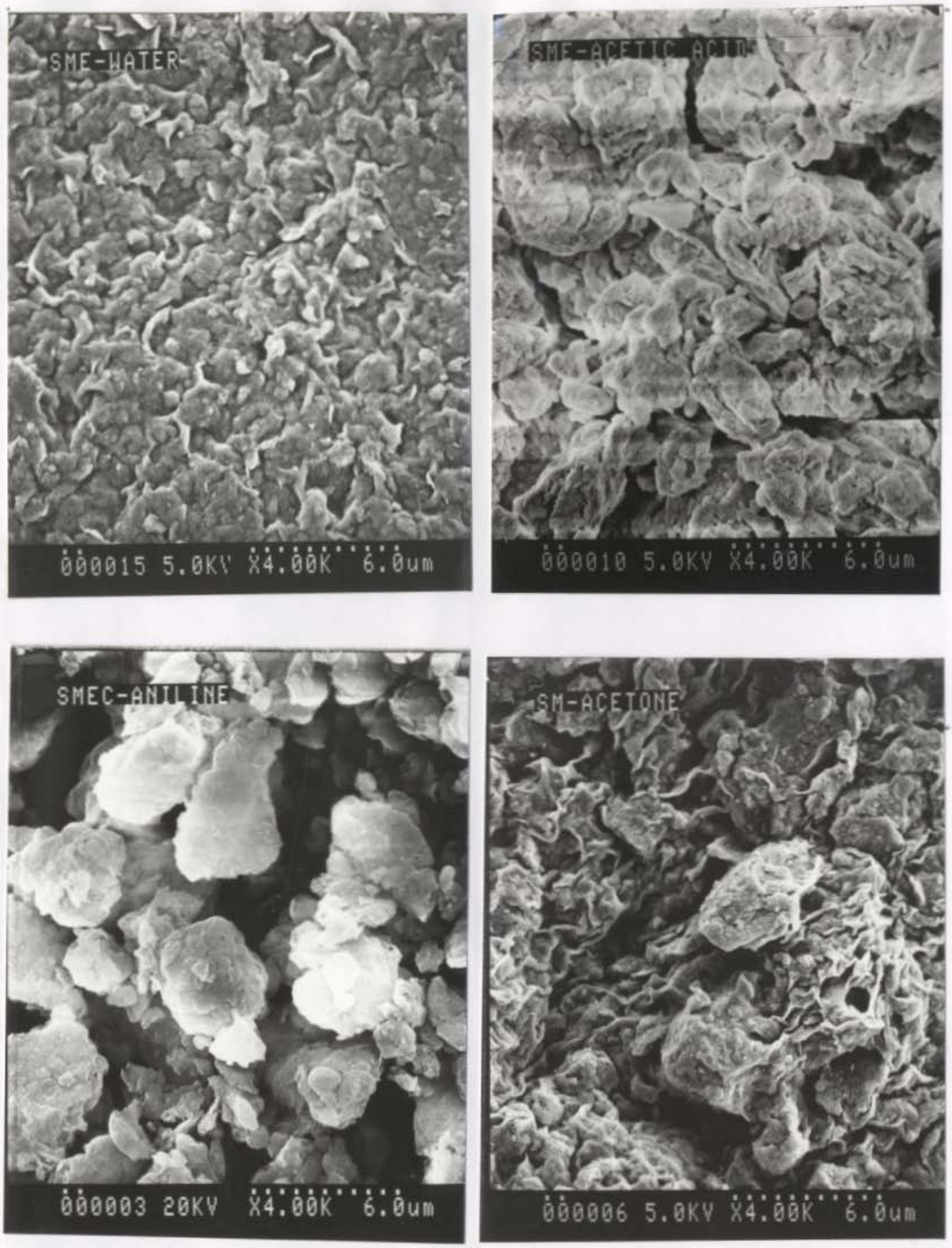


Figure 4.13: Photomicrographs of Smectite – (a) Water (b) Acetic acid (c) Aniline (d) Acetone

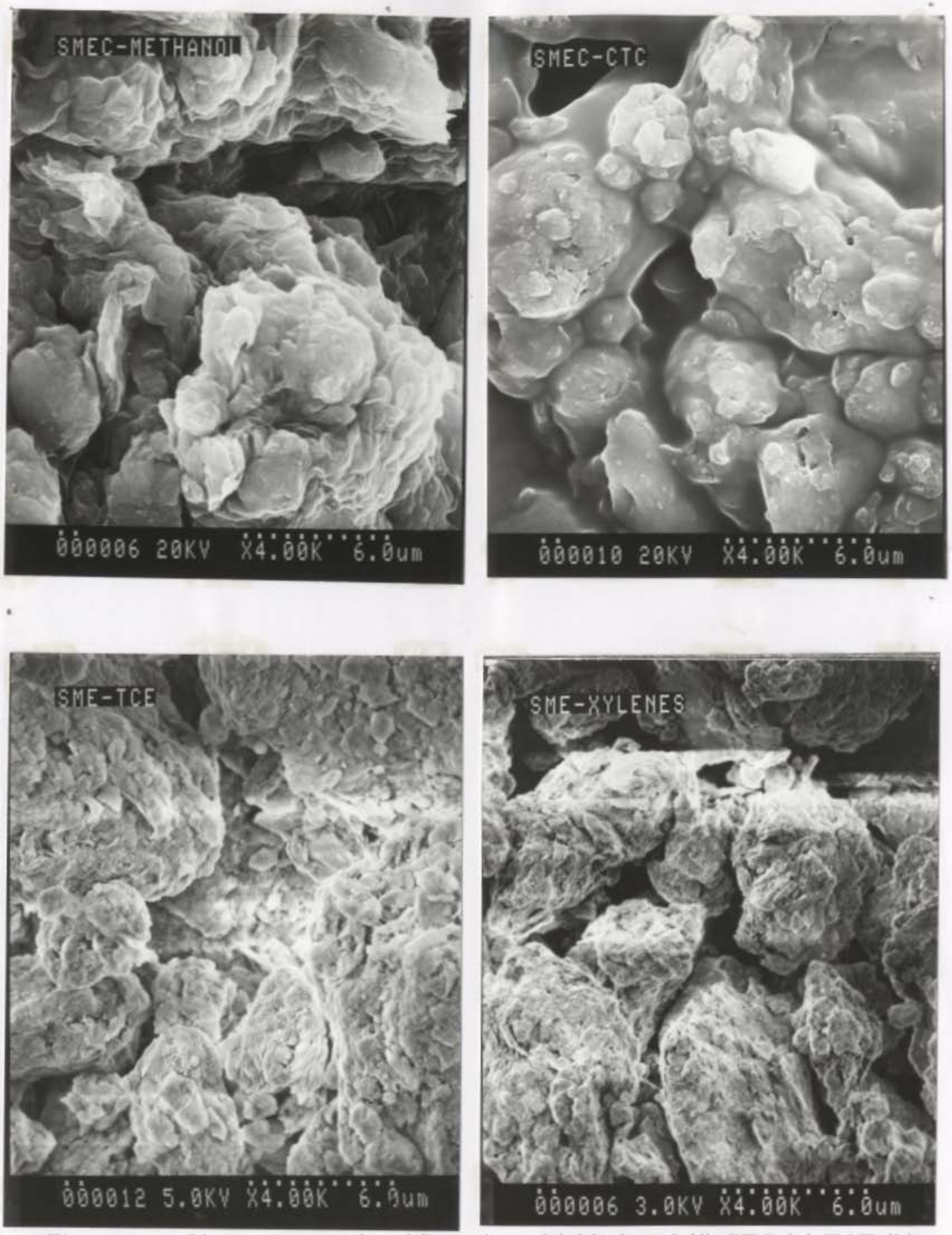


Figure 4.14: Photomicrographs of Smectite – (e) Methanol (f) CTC (g) TCE (h) Xylene

flocculation, within 5 minutes of sedimentation test initiation, was observed in all clays when the liquids used were nonpolar. These liquids also had very low dielectric constants (ranging from 2 to 6) compared to the other permeants used in this investigation (ranging from 2 to 80).

Flocculation of mineral grains seems to be the mechanism responsible for changes in the microfabric as evident from the micrographs. It was seen that the nonpolar liquids caused over 100% increase (kaolinite, illite) or decrease (smectite) in liquid limit. These findings seem to support the conclusions of Bowders and Daniel (1987) that liquids which affect sedimentation patterns and index tests affect the permeability. Clearly, current findings indicate that this concept may be applicable to changes in microfabric as well. Liquids which do not cause rapid flocculation in sedimentation tests or appreciable changes in liquid limit do not appear to alter the microstructure appreciably, although some evidence exists of aggregation formation. These liquids probably affect hydraulic conductivity by other mechanisms.

Chapter 5

Summary and Conclusions

This chapter summarizes the primary objectives and findings of this investigation. Conclusions drawn based on the experimental study and the implications of these findings for organic contaminant containment applications are also included in this final chapter.

5.1 Summary

The effects of organic liquids on various physical, hydraulic and microstructural properties of three clays were investigated in this study. The clays were chosen to represent the extremes in clay structure and properties. The organic liquids had

covered a wide range of species: acids, bases, neutral polar and neutral nonpolar. The correlation between tests such as sedimentation analyses, index property tests and permeability tests with changes in the microfabric was also studied. Changes in permeability were studied using a rigid wall permeameter. Scanning Electron Microscopy was used to study changes in the microfabric of the clays. Results indicate that both the sedimentation analyses and liquid limit tests can be used to provide a conservative estimate regarding the type of waste fluids that may alter significantly the intrinsic permeability and microstructure of the test clays. It is concluded that those liquids, which do not affect the sedimentation patterns or alter liquid limit values appreciably from baseline values obtained with the standard permeant water, will not affect the hydraulic conductivity or microstructure significantly. This is consistent with the findings of Bowders and Daniel (1987) with respect to hydraulic conductivity.

Changes in intrinsic permeability from baseline values are not significant for kaolinite when permeated with water miscible fluids, with only a slight trend towards an increase in intrinsic permeability. Increases of the order of two to three times the baseline values have been observed for the smectitic clay. These results are consistent with those of Green et al. (1981) and Uppot and Stephenson (1989) for their permeability studies. The apparent initial decrease in intrinsic permeability in the case of the liquids immiscible with water is thought to be due to the energy expended by these fluids in expelling the interstitial water. This

effect is mainly observed in the nonpolar liquids. The increase in permeability observed with aniline appears to be due to the ability of aniline to modify the structural arrangement of the clay particles at a microscopic as well as at a macroscopic level.

From the micrographs, it is observed that acetic acid, acetone and methanol do not cause significant alterations to the microfabric of kaolinite and illite. No visible cluster formations, shrinkage or cracks were detected. Samples prepared with aniline, CTC, xylene and TCE show distinct clustering with large macropores. TCE and xylene have a similar influence on the grouping of particles. For CTC, clustering in a manner similar to fusion of domains is observed. The effects were found to be most significant in the electrochemically active smectite.

5.2 Conclusions

All the three clays that have been studied have hydraulic conductivities less than the EPA prescribed value (1×10^{-7} cm/s), even for compaction conditions much less than the maximum dry unit weight. They are, therefore eligible materials for construction of liners for hazardous chemical waste facilities. An investigation of the changes in the intrinsic permeability and microstructure of the three clays when exposed to organics leads to the following conclusions:

1. Smectite has the lowest initial intrinsic permeability but is the most affected by changes in the composition of the test fluid. Kaolinite has a high initial permeability but is more resistant to changes. Illite displays intermediate behavior as compared to kaolinite and smectite.

2. Nonpolar liquids that have a very low dielectric constants (less than 10) cause important structural alterations in all three clays. Aggregation of clay particles resulting in huge macropore formation indicates that appreciable intrinsic permeability increases can be expected in the regions of the liner materials that are exposed to these liquids.

3. Liquids which are immiscible with water have to expend appreciable energy before they can replace the interstitial water and react with the liner material. This can be beneficial in reducing contaminant transport by advection.

4. Preliminary testing methods such as sedimentation analyses and index property tests can be used as indicators of the types of liquids that may alter the intrinsic permeability and microstructure.

Chapter 6

References

Acar, Y.B., Hamidon, A., Field, S. and Scott, L. (1985). The Effect of Organic Fluids on Hydraulic Conductivity of Compacted Kaolinite. *ASTM STP 874*, pp 171–187.

Anderson, D. (1982). Does Landfill Leachate Make Clay Liners More Permeable? *Civil Engineering – ASCE*, pp 66–69.

Anderson, D., Brown, K., and Green, J. (1981). Organic Leachate Effects on the Permeability of Clay Liners. *National Conference on Management of Uncontrolled Hazardous Waste Sites, Wash., D.C.*, pp 223–229.

Anderson, D., Brown, K., and Thomas, J. (1985). Conductivity of Compacted

Clay Soils to Water and Organic Liquids. *Waste Management and Research*, 3(4):339 349.

Bailey, S. (1963). Polymorphism of the Kaolin Minerals. *Am. Miner.*, 48:1196 1209.

Bowders, J. and Daniel, D. (1987). Hydraulic Conductivity of Compacted Clay to Dilute Organic Chemicals. *Journal of Geotechnical Engineering*, 113(12):1432 1448.

Bowders, J., Daniel, D., Broderick, G., and Liljestrand, H. (1986). Methods for Testing the Compatibility of Clay Liners with Landfill Leachate. *Hazardous and Industrial Solid Waste Testing: Fourth Symposium, ASTM STP 886, Philadelphia*, pp 233 250.

Boynton, S. and Daniel, D. (1985). Hydraulic Conductivity Tests on Compacted Clay. *Journal of Geotechnical Engineering*, 111(4):465 478.

Brindley, G. and Robinson, K. (1946). The Structure of Kaolinite. *Mineralogy Magazine*, 27:242 253.

Brown, K. and Anderson, D. (1983). Effects of Organic Solvents on the Permeability of Clay Soils. *Solid and Hazardous Waste Res. Div., USEPA 600/S2 - 83 - 016, Cincinnati, Ohio.*

Brown, K., Thomas, J., and Green, J. (1984). Permeability of Compacted Soils to Solvent Mixtures and Petroleum Products. *Land Disposal of Hazardous Waste : Proceedings of the Tenth Annual Research Symposium*. *USEPA*, pp 124 -137.

Brunelle, T., Leroy, R., and Meyer, C. (1987). Methods for Testing the Compatibility of Clay Liners with Landfill Leachate. *Geotechnical Practice for Waste Disposal.*

Budhu, M., Giese, R.F., Campbell, G. and Baumgrass, L. (1991). The Permeability of Soils with Organic Fluids. *Canadian Geotechnical Journal*, 28:140-147.

Carpenter, G. and Stephenson, R. (1986). Permeability Testing in the Triaxial Cell. *Geotechnical Testing Journal*, 9(1):3-9.

Daniel, D. and Liljestrand, H. (1984). *Effects of Landfill Leachates on Natural Liner Systems.* Report GR83-6, Geotechnical Engineering Center, University of Texas, Austin.

Daniel, D., Trautwein, S., Boynton, S., and Foreman, D. (1984). Permeability Testing with Flexible Wall Permeameters. *Geotechnical Testing Journal*, 7(3):113 122.

Deer, W., Howie, R., and Zussman, J. (1966). *An introduction to the Rock-Forming Minerals.* Longman Group Limited, London.

Edil, T. and Erickson, A. (1985). Procedure and Equipment Factors Affecting Permeability Testing of a Bentonite-Sand Liner Material. *Hydraulic Barriers in Soil and Rock, ASTM STP 874, Philadelphia*, pp 155 170.

Fernandez, F. and Quigley, R. (1985). Hydraulic Conductivity of Natural Clays Permeated with Simple Liquid Hydrocarbons. *Canadian Geotechnical Journal*, 22(2):205-214.

Fernandez, F. and Quigley, R. (1988). Viscosity and Dielectric Constant Controls on the Hydraulic Conductivity of Clayey Soils Permeated with Water-Soluble Organics. *Canadian Geotechnical Journal*, 25:582 589.

Fetter, C. (1993). *Contaminant Hydrogeology*. Macmillan, New York.

Foreman, D. and Daniel, D. (1984). Effects of Hydraulic Gradient and Method of Testing on the Hydraulic Conductivity of Compacted Clay to Water, Methanol and Heptane. *Land Disposal of Hazardous Waste : Proceedings of the Tenth Annual Research Symposium at Ft. Mitchell, Kentucky*, pp 138 144.

Foreman, D. and Daniel, D. (1986). Permeation of Compacted Clay with Organic Chemicals. *ASCE Journal of Geotechnical Engineering*, 112(7):669 681.

Freeze, R. and Cherry, J. (1979). *Groundwater*. Prentice-Hall, Inc.

Gilligan, E. and Clemence, S. (1984). Fabric and Engineering Behaviour of

Organic-Saturated Clays. *Bulletin of the Association of Engineering Geologists*, 21:515–529.

Goldman, L., Greenfield, L., Damle, A., Kingsbury, G., Northeim, C., and Truesdale, R. (1990). *Clay Liners for Waste Management Facilities : Design, Construction and Evaluation*. Noyes Data Corporation, New Jersey.

Green, W., Lee, G., and Jones, R. (1981). Clay-Soils Permeability and Hazardous Waste Storage. *Journal of Water Pollution Control Federation*, 53(8):1347–1354.

Green, W., Lee, G., Jones, R., and Pallt, T. (1983). Interaction of Clay Soils with Water and Organic Solvents : Implications for the Disposal of Hazardous Wastes. *Environmental Science and Technology*, 17(5):278–282.

Griffin, R., Shimp, N., Steele, J., Ruch, R., White, W., and Hughes, G. (1976). Attenuation of Pollutants in Municipal Landfill Leachate by Passage Through Clay. *Environmental Science and Technology*, 10(13):1262–1267.

Grim, R. (1968). *Clay Mineralogy*. McGraw Hill, New York.

Lagaly, G. (1984). Clay-Organic Interactions. *Phil. Trans. R. Soc. London. A*, 311:315–332.

Mesri, G. and Olson, R. (1971). Mechanisms Controlling the Permeability of Clays. *Clays and Clay Minerals*, 19:151–158.

Miller, D. (1980). *Waste Disposal Effects on Ground Water.* Premier Press, Berkeley, California.

Mitchell, J. (1976). *Fundamentals of Soil Behavior.* John Wiley and Sons, Inc., New York.

Mitchell, J., Hooper, D., and Campanella, R. (1965). Permeability of Compacted Clay. *Journal of the Soil Mechanics and Foundations Division*, 91:41 66.

Mitchell, J. and Madsen, F. (1987). Chemical Effects on Clay Hydraulic Conductivity. *Geotechnical Practice for Waste Disposal*, pp 87 116.

Olson, R. and Daniel, D. (1981). Measurement of Hydraulic Conductivity of Fine Grained Soils. *Permeability and Groundwater Contaminant Transport, ASTM STP 746, Philadelphia*, pp 18 64.

Peterson, N. (1983). 1983 Survey of Landfills. *Waste Age*, pp 37 40.

Pusch, R. (1982). Mineral-Water Interactions and Their Influence on the Physical Behavior of Highly Compacted Sodium Bentonite. *Canadian Geotechnical Journal*, 19:381 387.

Raussell-Colom, J. and Serratosa, J. (1987). *Chemistry of Clays and Clay Minerals.* Mineralogical Society Monograph No. 6, London.

Ross, C. and Kerr, P. (1931). The Kaolin Minerals. *Prof. Pap. U.S. Geol. Surv.*, 165:151 180.

Schramm, M. (1981). *Permeability of Soils to Four Organic Liquids and Water.* Department of Hydrology and Water Resources, University of Arizona.

Shackelford, C. (1994). Waste-Soil Interactions that Alter Hydraulic Conductivity. *Hydraulic Conductivity and Waste Containment Transport in Soil, ASTM STP 1142, American Society for Testing and materials*, pp 111 169.

Theng, B. (1974). *The Chemistry of Clay Organic Interactions.* John Wiley and Sons, Inc., New York.

Tchobanoglous. (1993) *Integrated Solid Waste Management:Engineering Principles and Management Issues.* McGraw-Hill, New York.

Uppot, J. and Stephenson, R. (1989). Permeability of Clays under Organic Permeants. *Journal of Geotechnical Engineering*, 115(1):114–131.

Weast, R. (1975). *CRC Handbook of Chemistry and Physics.* CRC Press, Ohio.

Yong, R.N. and Sheeran, D.E. (1973). Fabric Unit Interaction and Soil Behavior. *Proceedings of the International Symposium on Soil Structure, Gothenburg, Sweden*, 176 183.

Appendix A

Grain Size Analysis

Grain size distribution plots are shown in Figures A.1, A.2 and A.3.

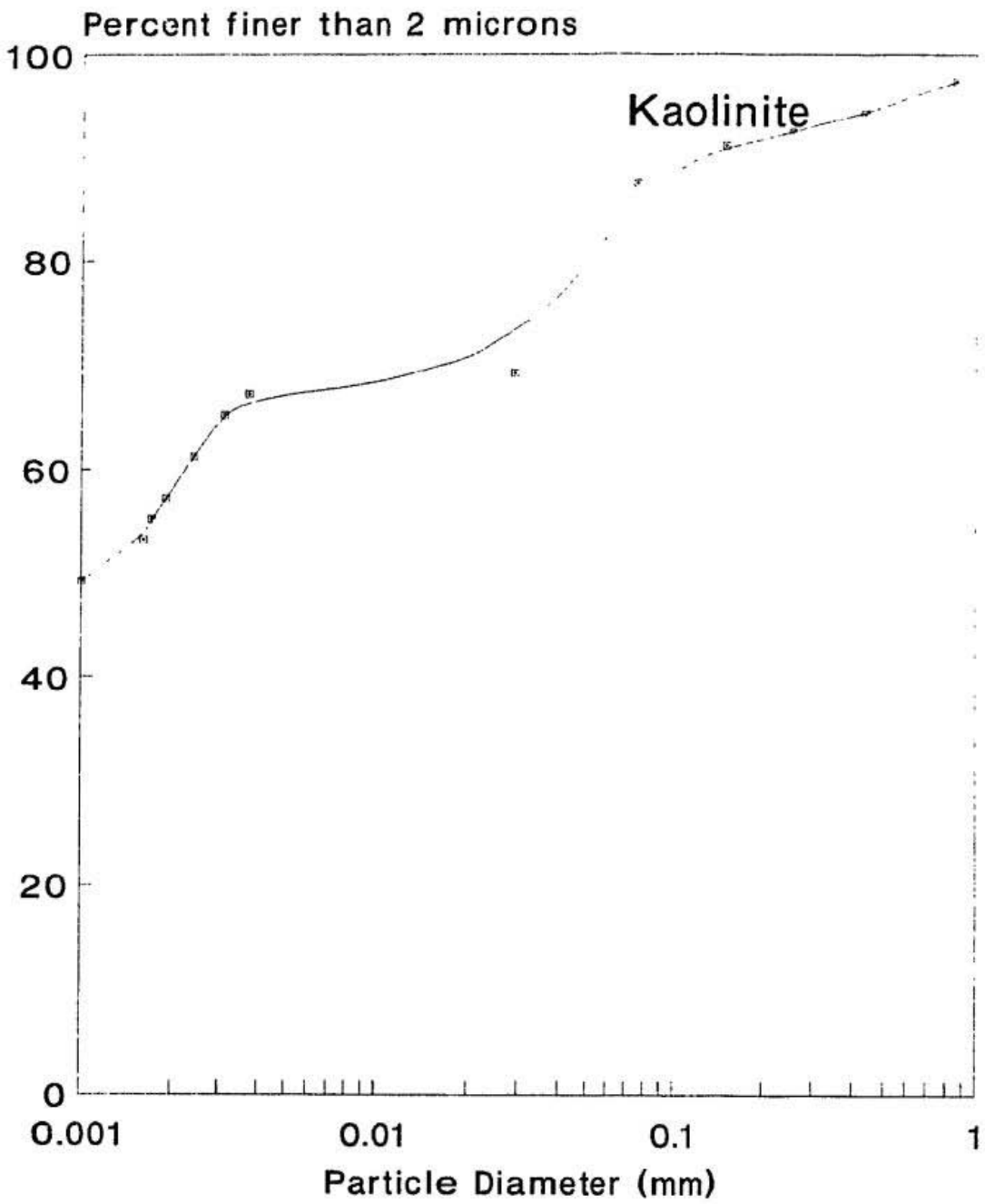


Figure A.1: Grain Size Distribution - Kaolinite

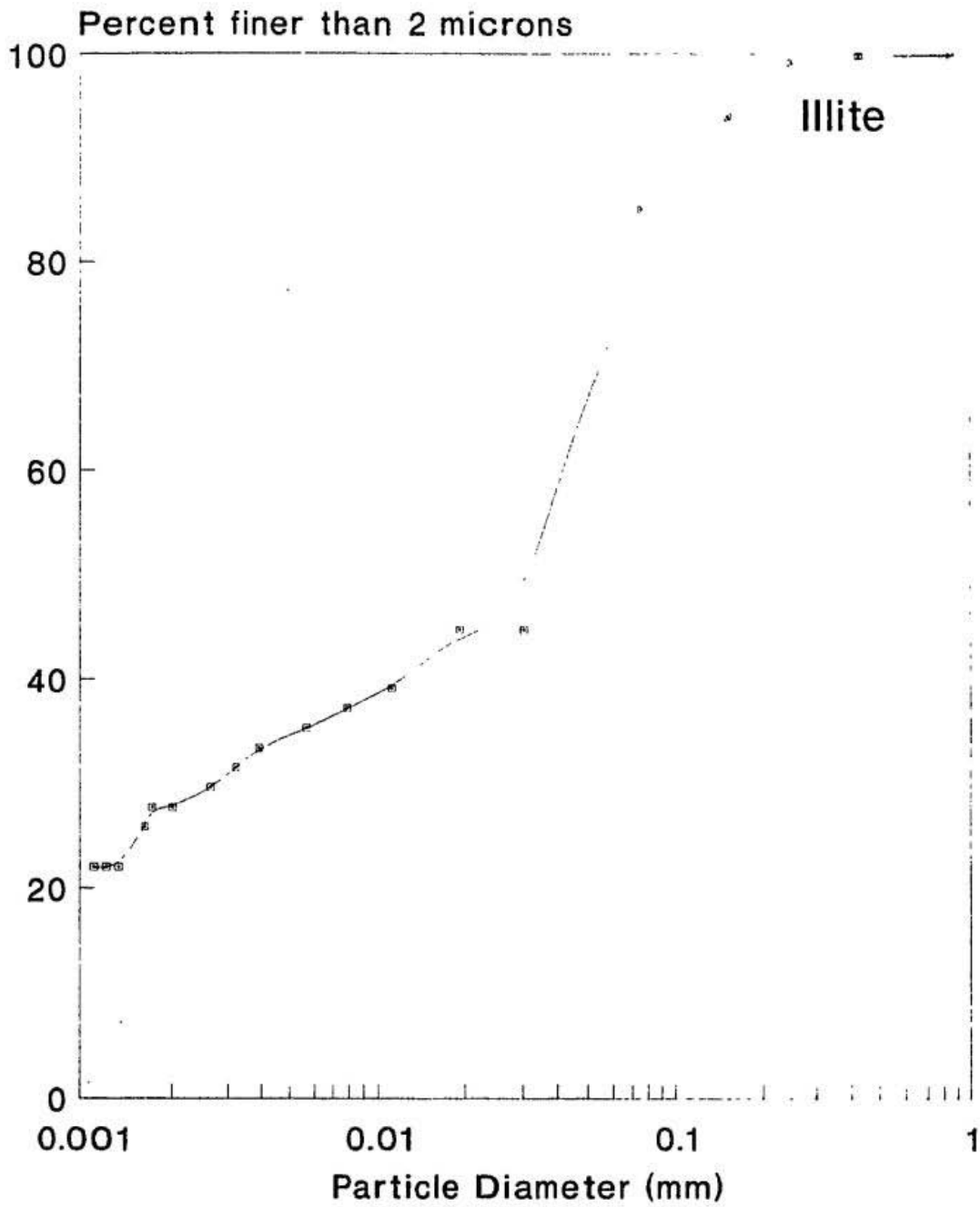


Figure A.2: Grain Size Distribution – Illite

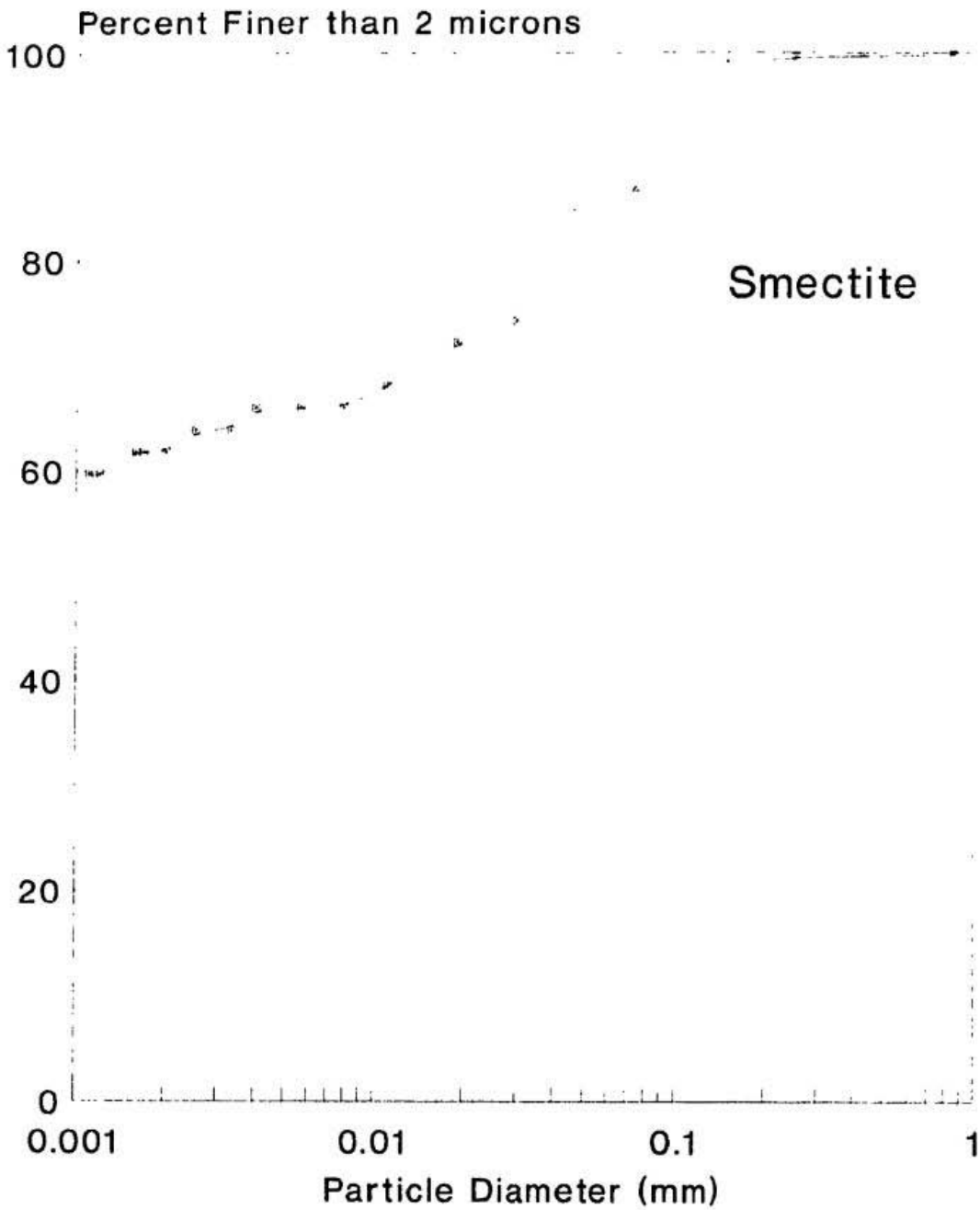


Figure A.3: Grain Size Distribution - Smectite

Appendix B

Atterberg Limits Tests

Liquid limit plots for kaolinite, illite and smectite are shown in Figures B.1, B.2 and B.3 respectively.

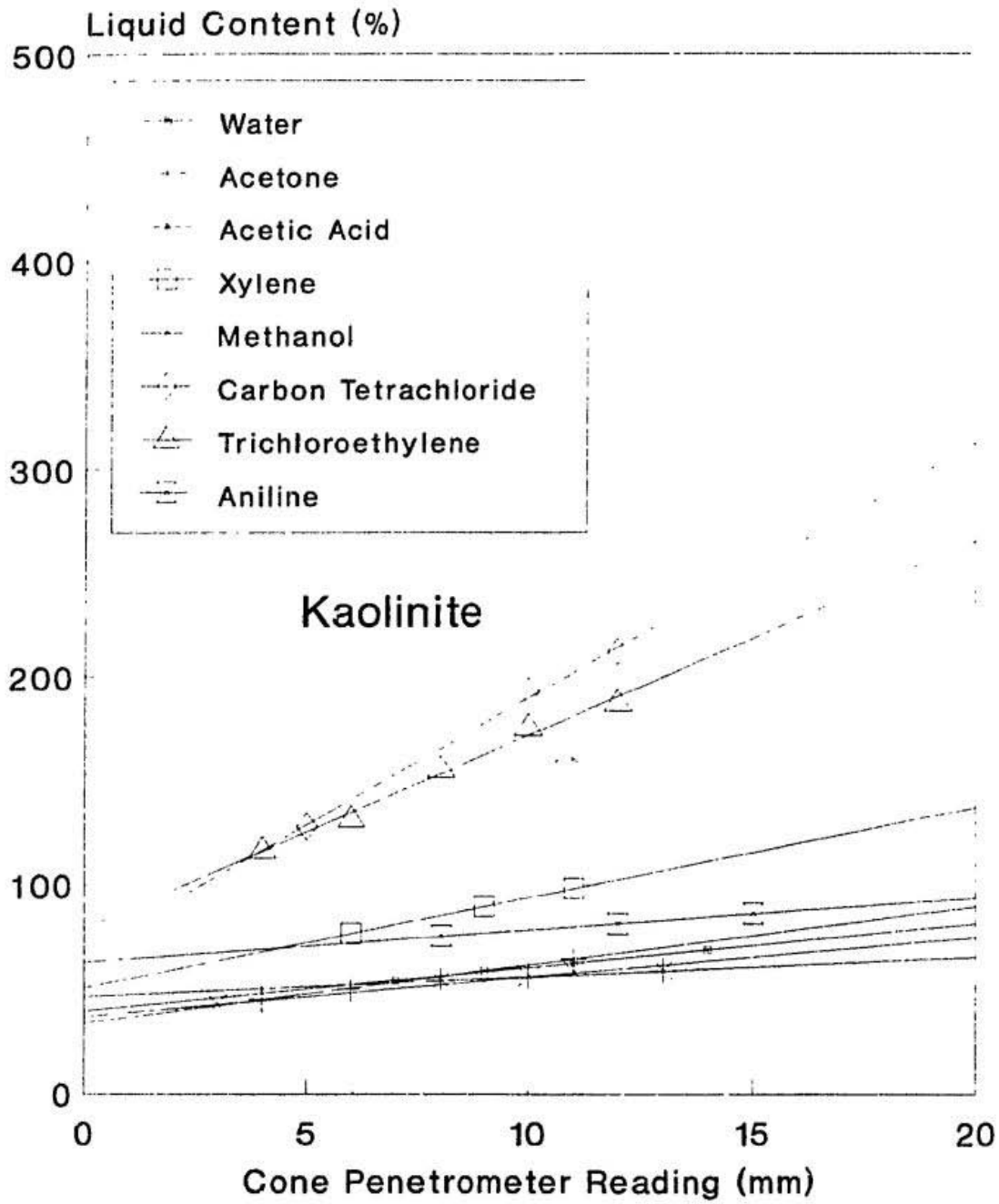


Figure B.1: Liquid Limit Profiles for Kaolinite

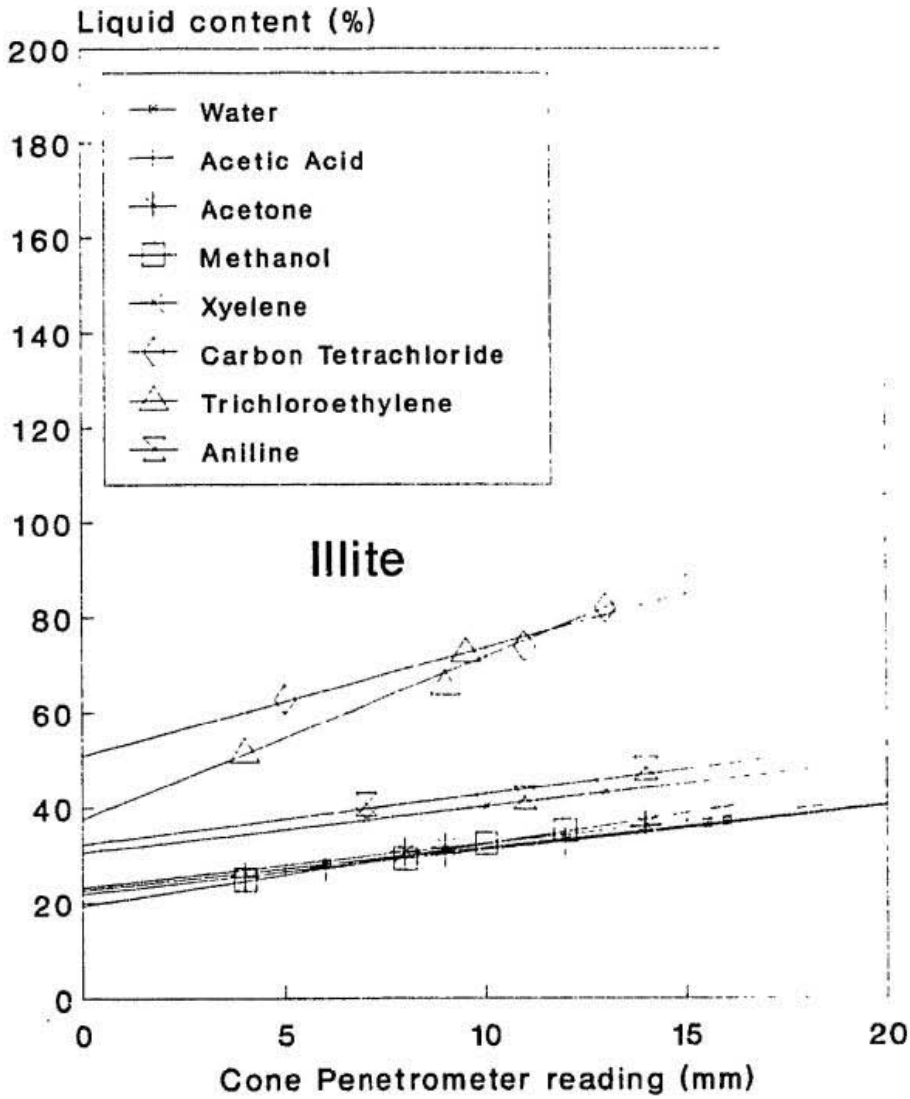


Figure B.2: Liquid Limit Profiles for Illite

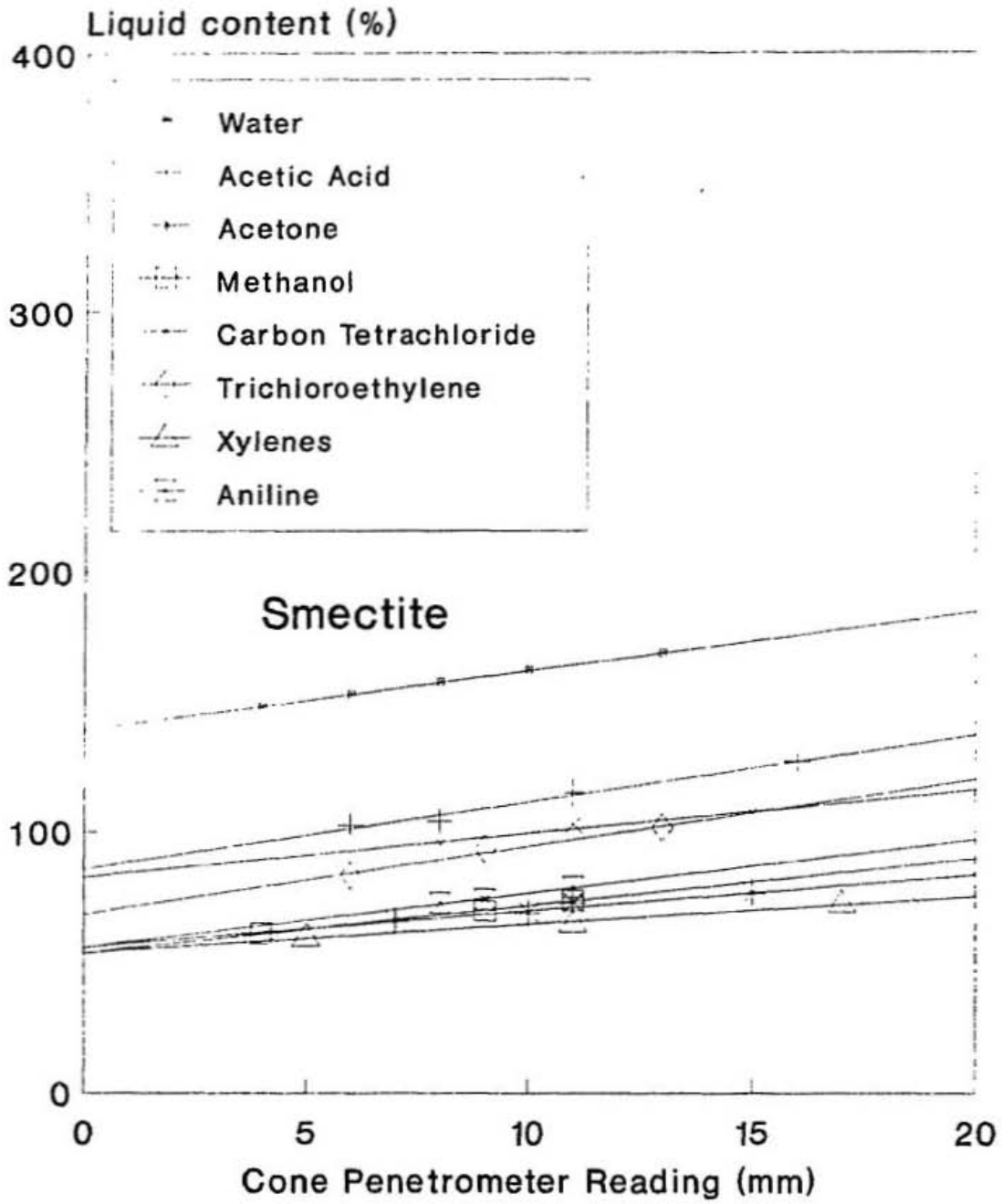


Figure B.3: Liquid Limit Profiles for Smectite

Appendix C

Compaction Tests

Moisture content - dry density plots obtained using Standard Proctor's tests (ASTM, 698-70) are shown in Figures C.1, C.2 and C.3 for kaolinite, illite and smectite respectively.

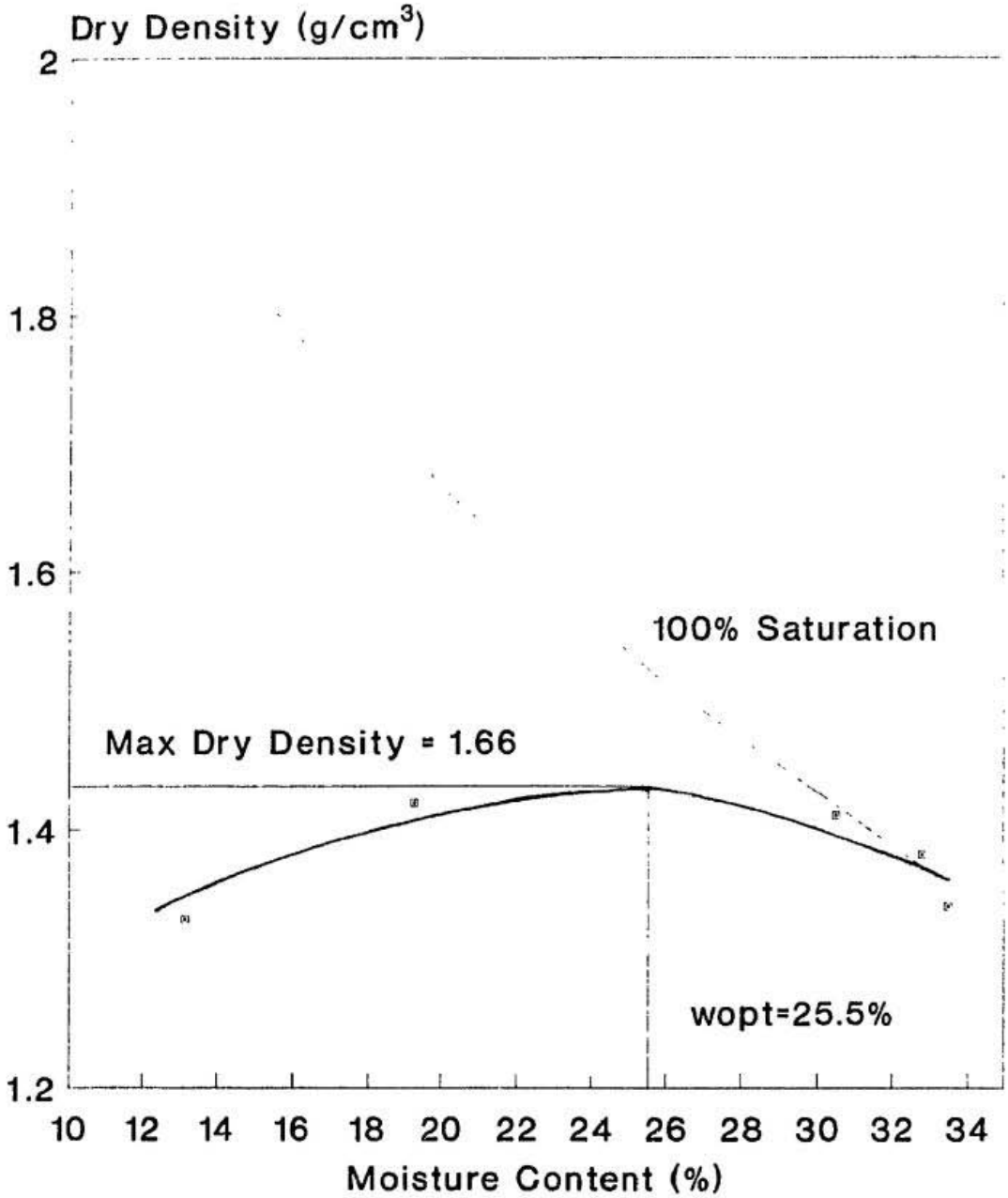


Figure C.1: Moisture Content - Dry Density Plots for Kaolinite

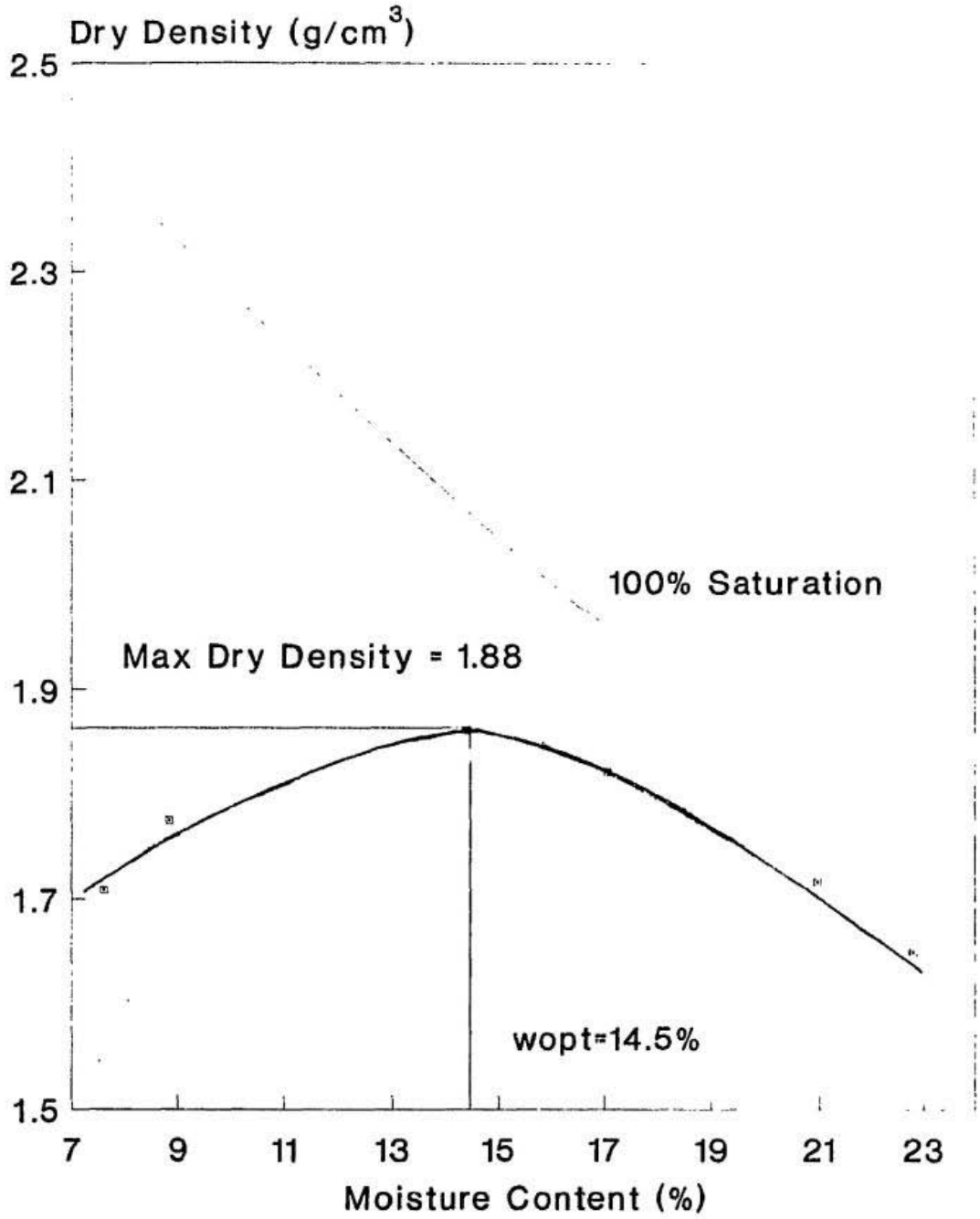


Figure C.2: Moisture Content - Dry Density Plots for Illite

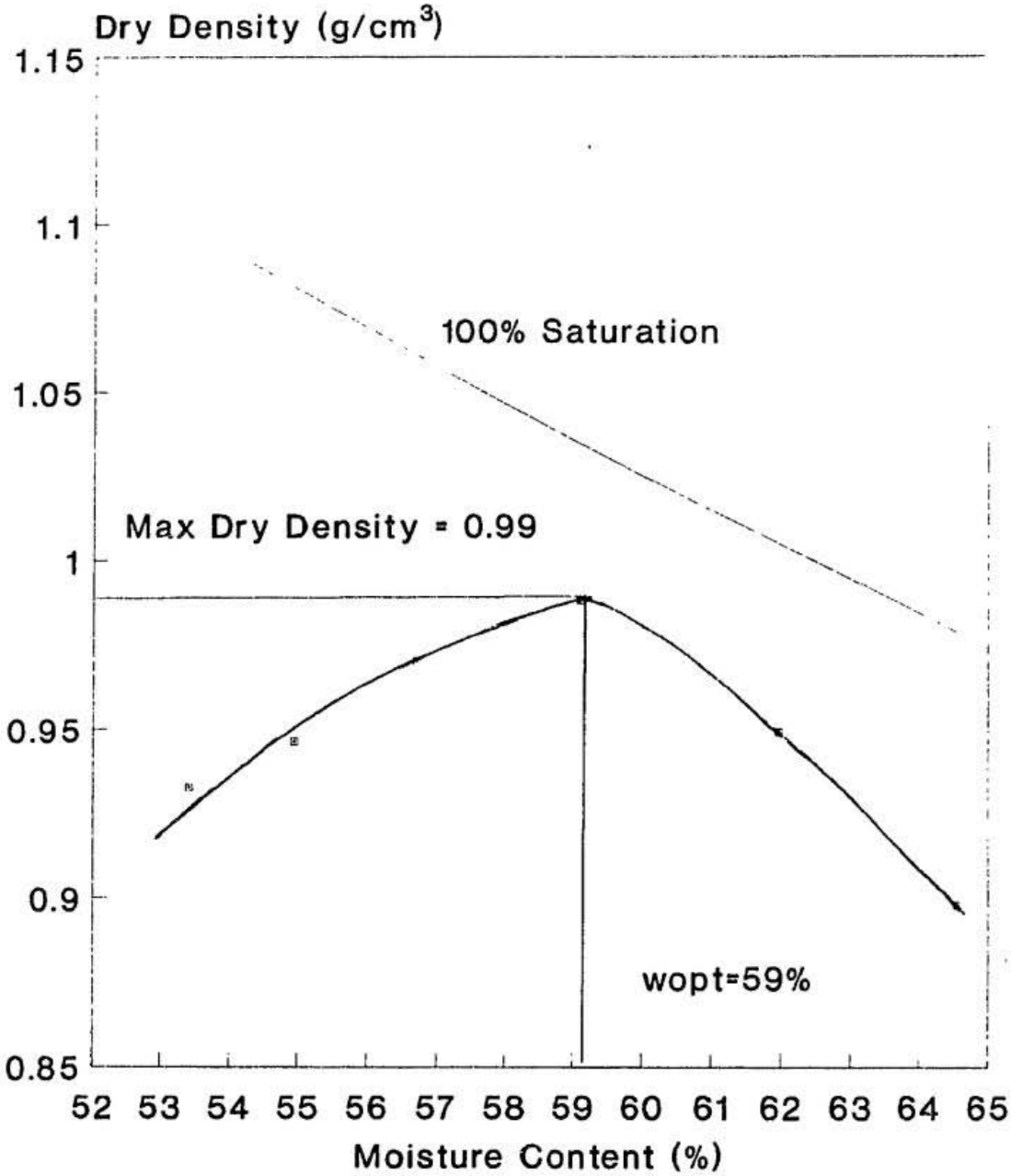


Figure C.3: Moisture Content - Dry Density Plots for Smectite

Appendix D

X-Ray Diffraction Studies

Samples for X-Ray diffraction analysis were prepared as follows:

- Untreated Samples: A suspension containing 10 mg of clay per ml of distilled water was prepared. 2 ml of the suspension was allowed to dry in air on a petrographic slide ($4.6cm \times 2.6cm$) at room temperature. The same procedure was followed for all the three clays. The dried samples were scanned using the X Ray Diffractometer (XRD) as described in section 3.2.2.

- Treated Samples

    1. Glycerol Treatment: This method was adopted for illite and smectite clays only. The clay sample, prepared as for untreated samples was

allowed to stand in a dessicator saturated with glycerol vapour. The clay was left in the dessicator for 48 hours to ensure adsorption of glycerol onto the clay surface. The dried samples were then analyzed as before using the XRD.

2. Heat Treatment:

   - For kaolinite: The dried untreated sample slide was heated to about $550°C$ in a muffle furnace for an hour. The heat treated samples were then analyzed as before.
   - For illite and smectite: The glycerol saturated samples were heated to about $550°C$ in a muffle furnace for an hour and the heat treated samples are analyzed. The diffractograms are given in Figures D.1, D.2 and D.3 respectively.

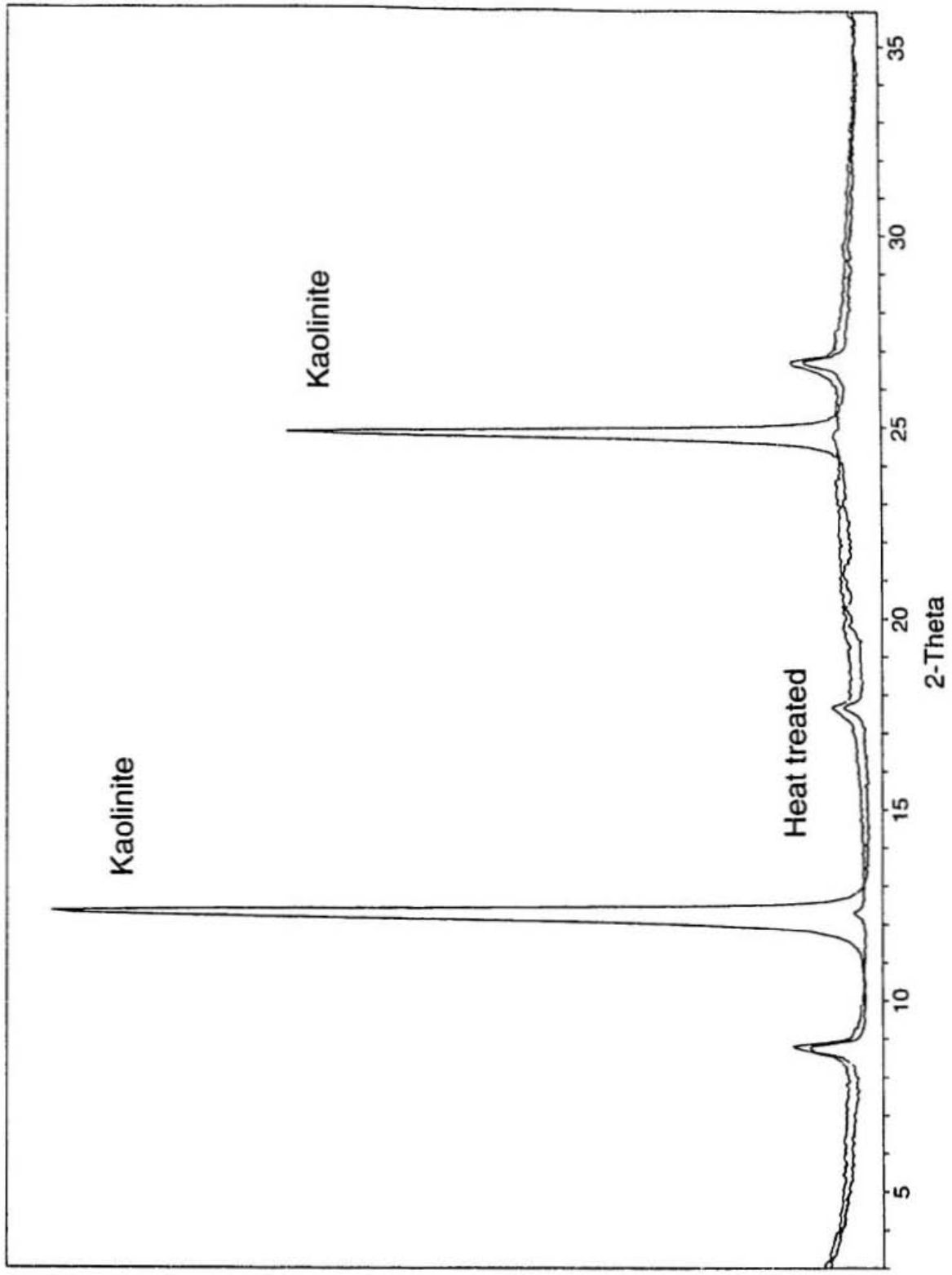


Figure D.1: X Ray Diffractograms - Kaolinite

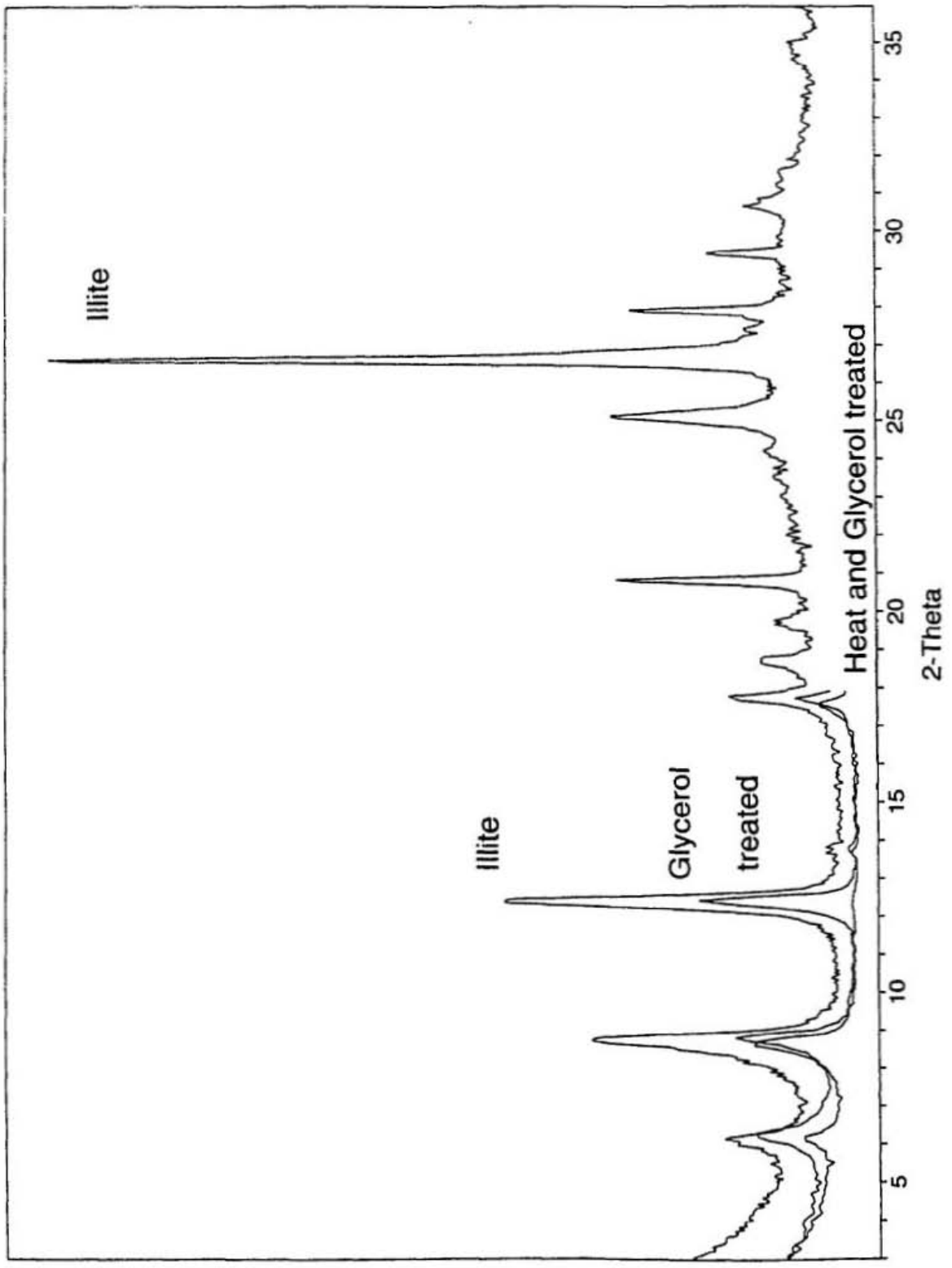


Figure D.2: X Ray Diffractograms – Illite

Figure D.3: X Ray Diffractograms - Smectite

Appendix E

Chemical Tests - Cation Exchange Capacity

Clays have been analyzed for Cation Exchange Capacity using the ammonium acetate method as follows: The ammonium acetate solution was prepared by diluting 77.1 g of ammonium acetate to 1 L in a volumetric flask with distilled water and adjusting the pH to 7. Four grams of air-dried soil were weighed into a 50 ml plastic centrifuge tube. Samples were prepared in duplicate to ensure reproducibility of results. To each of the tubes, 33 ml of ammonium acetate solution was added to make up the volume to 40 ml. The tubes were then placed in a reciprocating shaker for about 2 hours. The filtrate was extracted through Whatman No. 2V filter paper and the filtrate was saved in a plastic vial for

analysis. After the required dilution (Dilution factor, D), the supernatant was analyzed for Na, K, Ca and Mg using a Perkin Elmer 2380 atomic absorption spectrophotometer (AAS) resulting in concentrations of the cations, C*. Addition of a lanthanum solution of 2000 ppm was required in both samples and standards to suppress interferences. The exchangeable cations (in meq/100g) are calculated using the equation E:

$$EC = \frac{C^* \times D \times V \times 100 \times \nu}{1000 \times WS \times AW} \qquad (E.1)$$

where

EC	=	Exchangeable cations (meq/100g)
C*	=	Concentration in exchangeable cation analyzed by AAS (ppm)
D	=	Dilution factor
V	=	Volume of ammonium acetate (ml)
ν	=	Cation valence
WS	=	Weight of dry soil (g)
AW	=	Atomic weight of cation (g)

The value in meq/100g for each of the cations was summed up to determine the CEC of the material. The values for C* and D obtained in the analyses are shown in the following data sheet.

PRELIMINARY TESTING OF CLAYS June 13, 1995

RESULTS OF CATION EXCHANGE CAPACITY TESTS
USING PERKIN ELMER 2380 ATOMIC ABSORPTION SPECTROPHOTOMETER

ABSORBANCE DATA FOR SODIUM

SAMPLE	ppm	ABSORBANCE	DILUTION
1	1	0.230	-
2	2	0.420	-
3	4	0.759	-
ILLITE	1.93	0.399	25
KAOLINITE	1.81	0.377	25
SMECTITE	3.41	0.659	300

ABSORBANCE DATA FOR POTASSIUM

SAMPLE	ppm	ABSORBANCE	DILUTION
1	1	0.122	-
2	3	0.379	-
3	5	0.610	-
ILLITE	3.06	0.378	25
KAOLINITE	0.93	0.117	25
SMECTITE	1.04	0.131	100

ABSORBANCE DATA FOR CALCIUM

SAMPLE	ppm	ABSORBANCE	DILUTION
1	1	0.033	-
2	3	0.092	-
3	5	0.152	-
ILLITE	3.96	0.121	100
KAOLINITE	2.58	0.080	10
SMECTITE	5.81	0.176	100

ABSORBANCE DATA FOR MAGNESIUM

SAMPLE	ppm	ABSORBANCE	DILUTION
1	0.1	0.040	-
2	0.3	0.111	-
3	0.5	0.180	-
ILLITE	0.37	0.136	100
KAOLINITE	0.16	0.060	50
SMECTITE	0.39	0.142	200

CATION EXCHANGE CAPACITY VALUES

SAMPLE	VALUE
KAOLINITE	3.8
ILLITE	22.1
SMECTITE	68.3

Figure E.1: Data Sheet - CEC Determination

Appendix F

Data on Permeability Test Specimens

Data on the water content, specific gravity, void ratio, pore volumes available for permeant flow, and degree of saturation of test specimens are listed in Tables F.1, F.2 and F.3 for kaolinite, illite and smectite respectively. Plots of intrinsic permeability (k) versus pore volumes of flow are also included in Figures F.1, F.2 and F.3 for kaolinite, illite and smectite respectively.

Table F.1: Data on Permeability Test Specimens - Kaolinite

Sample I.D.	Liquid Type	WC	DD	VR	P	DS
KA-AA-1	Acetic Acid	29.2	1.46	0.71	41.50	102.50
KA-AN-2	Aniline	44.1	1.20	1.08	51.84	102.07
KA-ACE-1	Acetone	36.6	1.32	0.89	47.09	102.38
KA-ME-1	Methanol	41.9	1.24	1.01	50.29	103.00
KA-CTC-1	Carbon Tetrachloride	39.0	1.28	0.95	48.71	102.33
KA-TCE-2	Trichloroethylene	44.5	1.20	1.09	52.05	101.99
KA-XY-1	Xylene	39.6	1.27	0.96	49.03	102.39

WC=Water Content (%)

DD=Dry Density (g/cm^3)

VR=Void Ratio

P=Porosity (%)

DS=Degree of Saturation (%)

Table F.2: Data on Permeability Test Specimens Illite

Sample I.D.	Liquid Type	WC	DD	VR	P	DS
IL-AA-1	Acetic Acid	28.2	1.62	0.81	44.86	101.96
IL-AN-1	Aniline	31.3	1.55	0.90	47.26	102.51
IL-ACE-1	Acetone	30.8	1.56	0.88	46.94	102.45
IL-ME-1	Methanol	27.8	1.64	0.79	44.14	103.54
IL-CTC-1	Carbon Tetrachloride	30.3	1.58	0.86	46.36	103.03
IL-TCE-2	Trichloroethylene	31.7	1.54	0.91	47.67	102.35
IL-XY-1	Xylene	30.3	1.58	0.87	46.39	102.96

WC=Water Content (%)

DD=Dry Density (g/cm^3)

VR=Void Ratio

P=Porosity (%)

DS=Degree of Saturation (%)

Table F.3: Data on Permeability Test Specimens Smectite

Sample I.D.	Liq... ! Type	WC	DD	VR	P	DS
SM-AA-1	Acetic Acid	120.1	0.65	3.11	75.64	102.85
SM-AN-3	Aniline	96.0	0.76	2.52	71.58	101.41
SM-ACE-1	Acetone	98.6	0.74	2.60	72.20	101.01
SM-ME-1	Methanol	116.5	0.66	3.03	75.17	102.39
SM-CTC-1	Carbon Tetrachloride	100.5	0.74	2.60	72.23	102.75
SM-TCE-2	Trichloroethylene	157.3	0.53	4.07	80.27	102.84
SM-XY-1	Xylene	114.1	0.67	2.97	74.78	102.35

WC=Water Content (%)

DD=Dry Density (g/cm^3)

VR=Void Ratio

P=Porosity (%)

DS=Degree of Saturation (%)

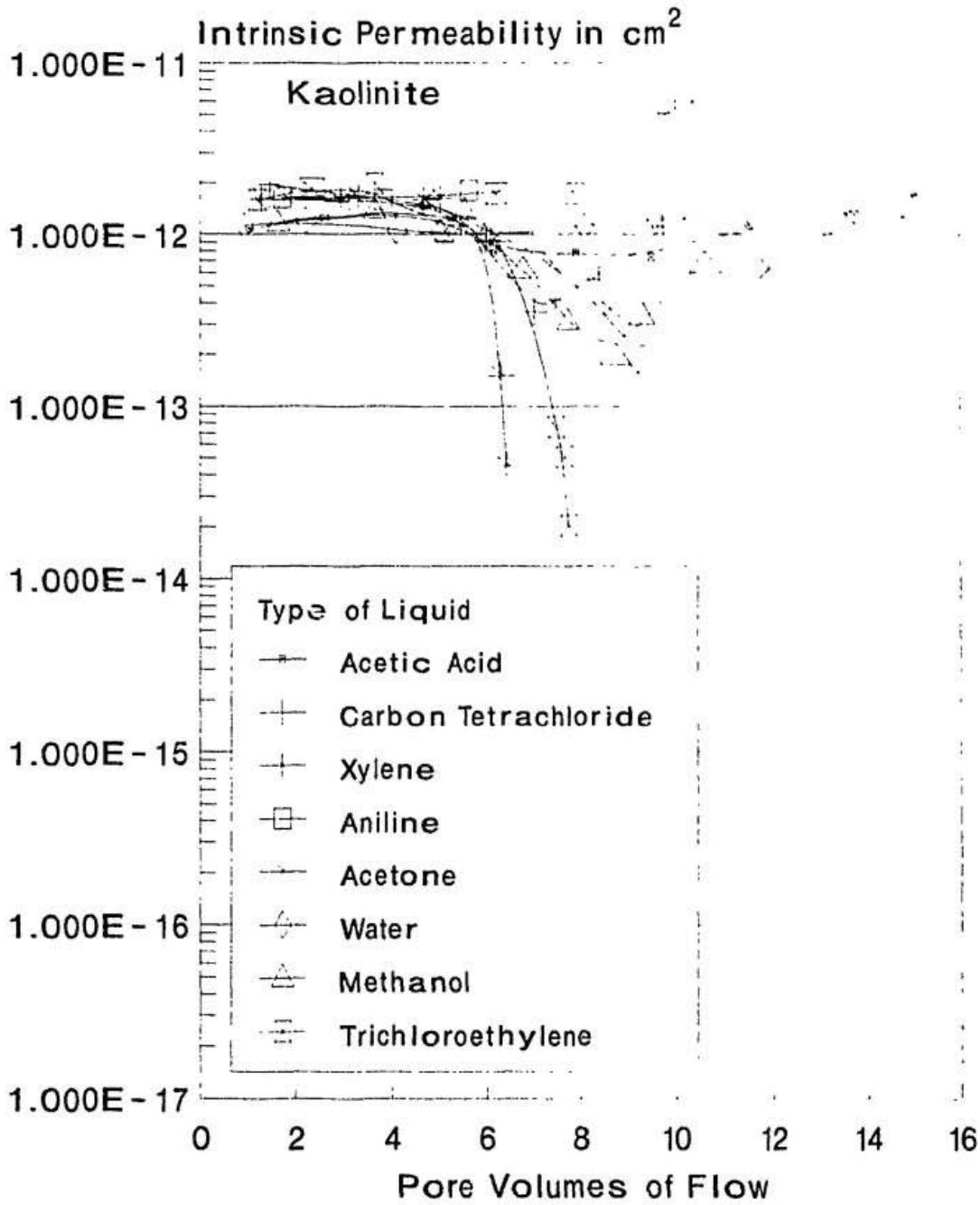


Figure F.1: Intrinsic Permeability Vs Pore Volumes Kaolinite

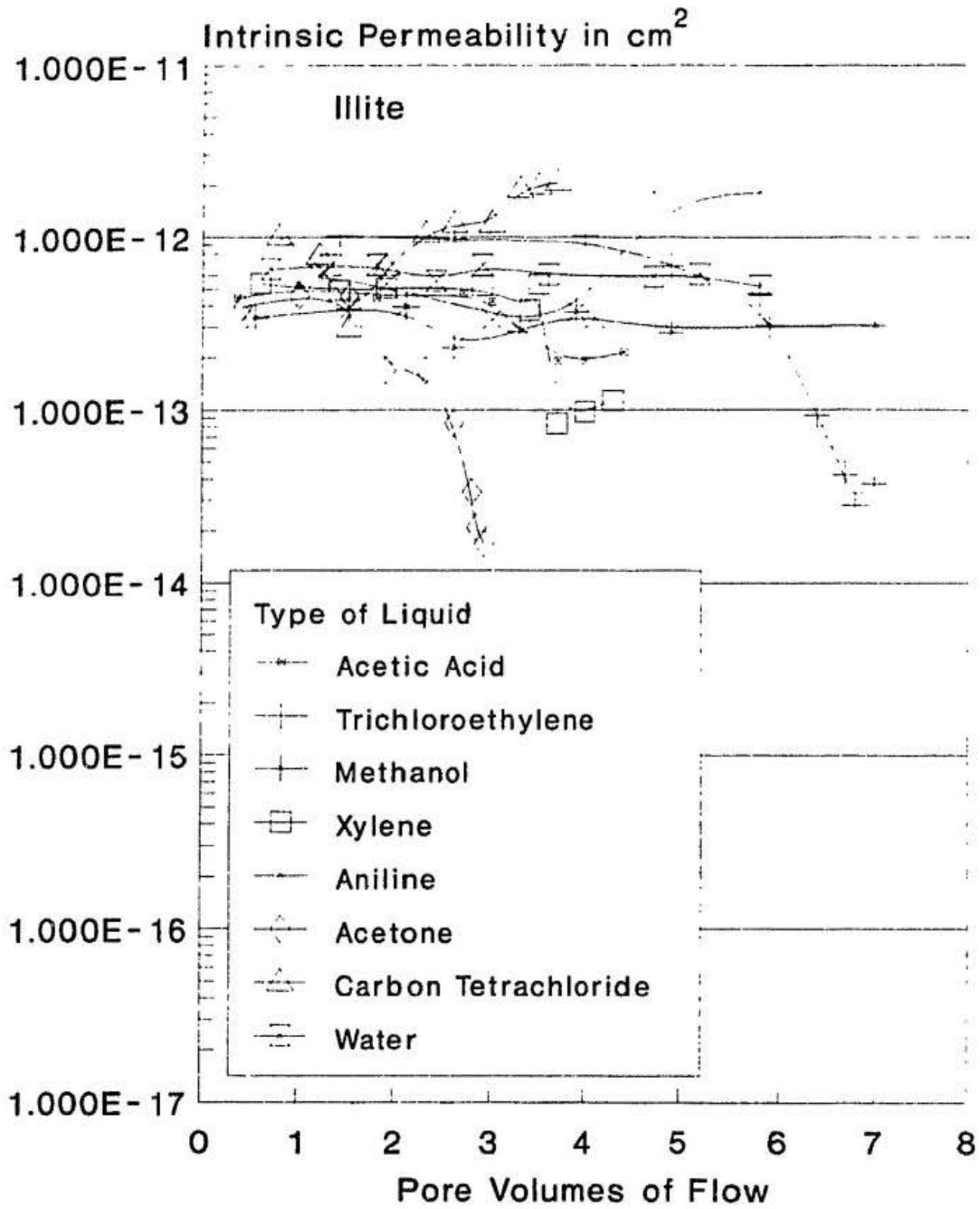


Figure F.2: Intrinsic Permeability Vs Pore Volumes – Illite

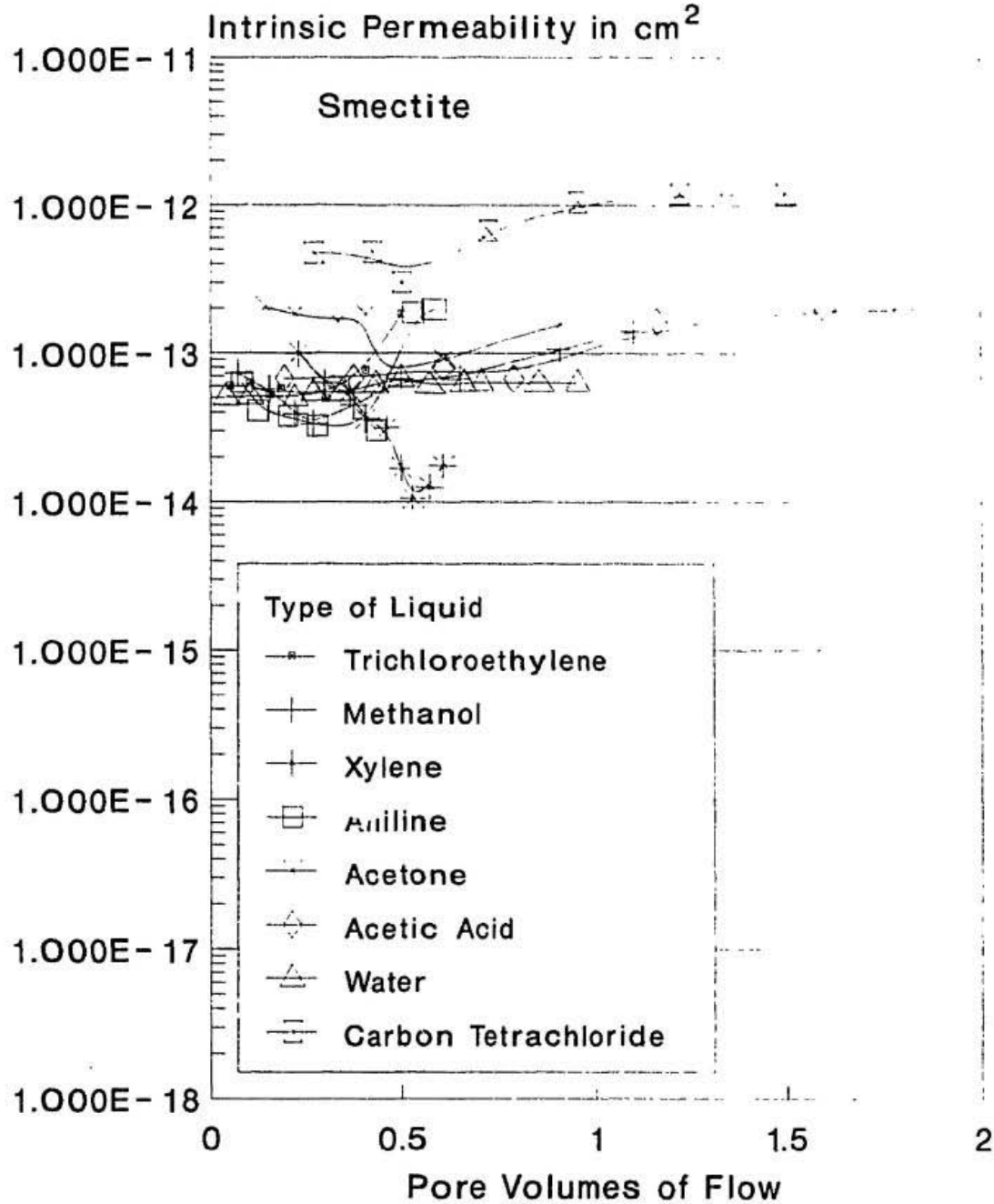


Figure F.3: Intrinsic Permeability Vs Pore Volumes - Smectite